NASA TECHNICAL REPORT

NASA TR R-355

NASA TR R-355

THREE-DIMENSIONAL COLLISION INDUCED VIBRATIONAL TRANSITIONS IN HOMOGENEOUS DIATOMIC MOLECULES

by C. Frederick Hansen and Walter E. Pearson

Ames Research Center
Moffett Field, Calif. 94035

0068426

1. Report No. NASA TR R-355	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle THREE-DIMENSIONAL COLLISION INDUCED VIBRATIONAL TRANSITIONS IN HOMOGENEOUS DIATOMIC MOLECULES		5. Report Date November 1970
		6. Performing Organization Code
7. Author(s) C. Frederick Hansen and Walter E. Pearson		8. Performing Organization Report No. A-3606
9. Performing Organization Name and Address NASA Ames Research Center Moffett Field, Calif. 94035		10. Work Unit No. 129-01-01-05-00-21
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C., 20546		13. Type of Report and Period Covered Technical Report
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The one-dimensional, semiclassical theory of vibrational transitions in diatomic molecules is extended to three dimensions. Simple exponential interaction potentials are assumed and are spherically averaged to determine the collision trajectory that defines the perturbation. For use over the range of temperatures where small perturbation theory applies, fully analytic approximations are derived for the cross sections, the rate coefficients, and the relaxation rates. Vibrational transitions (predominantly changes of one vibrational level) are found to be accompanied by simultaneous rotational transitions (predominantly changes of zero and two rotational levels) with the result that vibrational transition rates are increased by 50 percent or more.

The three-dimensional theory enables one to determine both the gradient and the magnitude of the potential, whereas only the gradient can be determined with one-dimensional theory. The theory can be fit to data reasonably well by appropriate choice of an "effective" interaction potential. This potential is considerably steeper and of shorter range than potentials appropriate for scattering. This is consistent with the concept that many interaction potentials exist for molecules, just as for atoms. We conclude that the steeper inner potentials are primarily responsible for vibrational transitions, whereas the outer potentials are primarily responsible for scattering.

17. Key Words (Suggested by Author(s)) Three-dimensional molecular collisions Vibrational transitions Transitional probabilities Vibrational cross sections	18. Distribution Statement Unclassified – Unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 71	22. Price* $3.00

A,$\overline{\text{A}}$ scale constants appearing in the interaction potential

B   rotational energy constant

b   impact parameter, or miss distance at infinite separation

E   energy

E_c characteristic energy, $\dfrac{m\omega^2 L^2}{2}$

$\hbar = \dfrac{h}{2\pi} = 0.6581\times10^{-15}$ (eV-sec)   Planck's constant

k   Boltzmann constant, $\dfrac{1}{11,605.4}$ (eV/°K)

L   characteristic range of the interaction potential

m   reduced mass of the collision

P,P(Δv,Δl)   probability that a single collision with energy E and miss
            distance b will cause a transition $(v,l) \to (v+\Delta v, l+\Delta l)$

r(t)   distance between the oncoming particle and the diatomic
            molecule

s   symmetry factor

S,S(Δv,Δl)   cross section for the transition whose probability is
            P(Δv,Δl) (see eq. (4))

T   temperature

t   time

U   interaction or perturbation potential

u   relative velocity of collision partners at infinite
            separation

$\overline{u} = \left(\dfrac{8kT}{\pi m}\right)^{1/2}$ average relative velocity at temperature T

$x = \dfrac{mu^2}{2kT}$ dimensionless collision energy

$\alpha(\Delta v)$ total rate coefficient for vibrational transition $v \to v+\Delta v$

$\alpha(\Delta v, \Delta l)$ rate coefficient for the transition $(v,l) \rightarrow (v+\Delta v, l+\Delta l)$

$\beta(\Delta v, \Delta l)$ perturbation matrix overlap integral (see eq. (42))

$$\delta = \frac{\rho_e}{2l}$$

μ reduced mass of the molecule

ρ separation distance of molecular nuclei

ρ_e equilibrium separation distance

σ distance of closest approach, or turning point (see fig. 1)

τ vibrational relaxation time (see eq. (6))

$\Psi(\rho, \theta, \phi, t)$ wave function of the rotating vibrating diatomic molecule

$\psi_{v,l,m}(\rho, \theta, \phi)$ time independent eigenfunction

$\omega, \omega(\Delta v, \Delta l)$ circular frequency

THREE-DIMENSIONAL COLLISION INDUCED VIBRATIONAL

TRANSITIONS IN HOMOGENEOUS DIATOMIC

MOLECULES

C. Frederick Hansen and Walter E. Pearson

Ames Research Center

SUMMARY

The one-dimensional, semiclassical theory of vibrational transitions in diatomic molecules is extended to three dimensions. Simple exponential interaction potentials are assumed and are spherically averaged to determine the collision trajectory that defines the perturbation. For use over the range of temperatures where small perturbation theory applies, fully analytic approximations are derived for the cross sections, the rate coefficients, and the relaxation rates. Vibrational transitions (predominantly changes of one vibrational level) are found to be accompanied by simultaneous rotational transitions (predominantly changes of zero and two rotational levels) with the result that vibrational transition rates are increased by 50 percent or more.

The three-dimensional theory enables one to determine both the gradient and the magnitude of the potential, whereas only the gradient can be determined with one-dimensional theory. The theory can be fit to data reasonably well by appropriate choice of an "effective" interaction potential. This potential is considerably steeper and of shorter range than potentials appropriate for scattering. This is consistent with the concept that many interaction potentials exist for molecules, just as for atoms. We conclude that the steeper inner potentials are primarily responsible for vibrational transitions, whereas the outer potentials are primarily responsible for scattering.

INTRODUCTION

Rates of vibrational transition produced by molecular collisions are involved in a number of gasdynamic problems. Vibrational modes of energy influence shock-wave structure, cause dispersion of sound, and are responsible for sizable variations in the equation of state, for example. The rate at which these modes are excited becomes important whenever it is comparable with the rate of change in gas properties generated by flow processes, sound waves, or other means.

Vibrational modes of the atmospheric gases are excited so little at normal temperatures that they can often be neglected entirely. However, aerodynamicists grew interested in vibrational relaxation with the development of supersonic flight; at that time, gas temperatures sufficiently high to excite

vibrational energy of air were produced in flow about vehicles and in shock tubes. Interest continued to grow as higher speed flight generated still higher temperatures and dissociation of molecules became an important energy sink in the flow, since it was soon recognized that the rates of dissociation and recombination were directly coupled to the vibrational transition rates (refs. 1-3). Recently, the gas laser has kindled still further interest in vibrational excitation and coupled rotational transitions, since the optical transition stimulated in some gas lasers occurs between a select pair of vibration-rotation levels, and the rate of population or depopulation of these levels by collision is one of the factors affecting laser operation.

So many studies of vibrational excitation have been made that it is hardly practical to recall all of them here. However, the principal methods of attack on the problem can be summarized by reference to a few selected papers. A classic paper by Landau and Teller (ref. 4), in 1936, analyzed the one-dimensional collision excitation of harmonic oscillator vibrations in connection with the dispersion of sound. Using simple, classical arguments about the form of the impulse produced in collision, they deduced that, to a first approximation, the vibrational relaxation rate should vary as $\exp[-(\theta/T)^{1/3}]$. Probably every set of measured vibrational relaxation rate data ever obtained for diatomic gases has been compared with their result, generally with reasonably good agreement (see refs. 5-9, for example). The Landau-Teller model was refined somewhat by Bethe and Teller (ref. 10) in 1945. In 1952, Schwartz, Slawsky, and Herzfeld (ref. 11) carried through a formal quantum treatment of energy exchange during one-dimensional collision between harmonic oscillators, based on the work of Zener (refs. 12 and 13) and Jackson and Mott (ref. 14). Takayanagi (ref. 15) independently published similar results. This work has been widely accepted as the most rigorous practical analytic approach to the problem. Schwartz and Herzfeld followed their study with a quantum treatment of three-dimensional collisions (ref. 16) based on the method of partial waves (ref. 17) in a manner similar to that of Takayanagi (ref. 15). Although they did not derive expressions for the cross sections - which, in principle, can be done with three-dimensional theory - they were able to conclude that the transition probabilities have the same functional form in the three-dimensional case as for the one-dimensional collisions. Treanor, Rich, and Rehm (ref. 18) used the one-dimensional Schwartz-Slawsky-Herzfeld theory to investigate effects of anharmonicity on vibration-vibration exchange.

An alternative approach is the semiclassical or impact parameter method in which the classical trajectory of motion between gas particles is used to obtain a time dependent perturbation potential; then transitions produced by this perturbation are calculated by quantum principles. Since the de Broglie wavelengths of heavy gas particles are normally much smaller than the scale-size of the potentials involved, the classical trajectory is a good approximation and the semiclassical results are potentially as accurate as needed for most practical purposes. In fact, Rapp (ref. 19) showed that a complete classical theory for the one-dimensional collision excitation of harmonic oscillators, from the ground state to the first excited level, gives exactly the same results as the complete quantum treatment by Herzfeld (ref. 20). However, in the more general case involving transitions between upper vibrational levels, or vibration-vibration exchange, it is necessary to evaluate

2

the wave function transition matrix elements to get correct results. Rapp and Sharp (refs. 21,22) used the semiclassical method to investigate the vibrational excitation produced by such high energy collisions that small perturbation theory fails, and Rapp and Golden (ref. 23) analyzed the resonant and near resonant vibration exchange with the semiclassical approach, all for one-dimensional collisions. Kerner (ref. 24) developed analytic expressions for the quantum mechanical transition probabilities of harmonic oscillators, subject to large perturbation forces where multiple quantum jumps occur, as functions of the energy transfer to a classical forced oscillator; and Treanor (refs. 25,26) showed that these solutions are consistent with the numerical solutions obtained by Sharp and Rapp (ref. 22). Of the three basic methods available (quantum, semiclassical, classical), the semiclassical method is usually simplest, although the classical collision trajectory used in it does not correctly conserve total energy in the collision.

Although one-dimensional collision studies lead to the functional form of the transition probabilities, it is necessary to make an educated guess for a "steric factor" or a "total cross section" in order to transform such transition probabilities into excitation cross sections and ultimately into rate coefficients. An absolute derivation of the cross sections must be based on a three-dimensional model of the collisions. Calvert and Amme (ref. 27) related the one-dimensional treatment to a three-dimensional model in an approximate way in order to arrive at a cross section, but did not fully consider the three-dimensional details of the collision process with coupled rotations. Mies and Shuler (ref. 28) extended Shuler and Zwanzig's treatment (ref. 29) of harmonic oscillator transitions to three dimensions, but for impulsive collisions that are recognized to be not very realistic, and by numerical methods that do not yield analytic relations. Thus, there is need for a further look at three-dimensional collision effects on vibrational transition.

The present paper extends the semiclassical method to three-dimensions and provides expressions for the vibrational transition cross sections and rate coefficients, including the effects of simultaneous rotational transitions, in terms of exponential interaction potential parameters. The method is then further extended to account for conservation of energy, and the effects of distortions in the classical trajectory, caused by reversible and irreversible transfer of energy to the vibrational mode, are assessed. The values of the potential parameters are found which best fit available experimental data for vibrational relaxation. Simple analytic approximations are deliberately extended as far as possible, even at the sacrifice of some accuracy, so that the general functional behavior of the cross sections and rate coefficients for vibrational transitions can be followed more readily.

GENERAL DISCUSSION OF THE PROBLEM

The problem considered here starts from a given interaction potential between colliding molecules and ends with the derivation of a rate coefficient and a relaxation time for vibrational transitions. The analysis proceeds by the following steps:

The interaction potential between a homogeneous diatomic molecule and an inert collision partner is assumed to be a simple superposition of exponentials

$$U = A \sum_i e^{-r_i/L} \qquad (1)$$

where the r_i are the distances between the inert gas particle and each atom of the target molecule. The constant A establishes the energy scale, and L is a characteristic length that establishes the potential gradients. In the more general case, where the vibrationally excitable molecule is inhomogeneous, separate constants A_i and L_i must be used for each atom of the target molecule, of course. According to results from scattering and viscosity measurements, or from quantum mechanical calculations - for the few cases where they are available - it appears that typical values of A are the order of several hundred eV, and that L is a fraction of an Angstrom.

The classical trajectory of relative motion between the gas particles is next determined for the spherically symmetric part of the interaction potential. This trajectory defines the impulse-like perturbation of the target molecule; the perturbation U is a function of time t, the coordinates of the molecule q (which represents a set of generalized coordinates q_i), the collision energy E, the impact parameter b (initial miss distance between the approaching gas particles), as well as the potential parameters A and L.

$$U = U(t,q,E,b,A,L) \qquad (2)$$

If the perturbation is small, or of very short duration, the probability of transition from state n to n' may be calculated according to small-perturbation-quantum theory. The calculation involves the integration of U, weighted by the product of the initial and final state wave functions, over all space and time. Thus, the variables t and q are eliminated, and the transition probability takes the form

$$P_{nn'} = P_{nn'}(E,b,A,L) \qquad (3)$$

Generally, small perturbation theory will suffice when comparisons can be made with experimental vibrational relaxation times. However, if the analysis must be extended to very high collision energies, the small perturbation result exceeds unity and the effects of coupling between adjacent states must be taken into account. With the approximations used by Kerner (ref. 24), the multiple transition probabilities that result from such large perturbations can be expressed as functions of the small perturbation transition rate from the ground state to the first excited state. Thus, in one form or another, the transition probabilities have a functional dependence as expressed in equation (3).

The collision cross section for transition is just the sum of the elements of cross section $2\pi b \, db$ weighted with their corresponding transition probabilities. Thus, cross section is a function of E, A, and L only

$$S_{nn'}(E,A,L) = \int_0^\infty P_{nn'} 2\pi b \, db \qquad (4)$$

4

The rate coefficient is obtained by averaging the cross section over all collision energies. In most cases, collision energies have a Boltzmann distribution, and the rate coefficient may be expressed as

$$\alpha_{nn'}(T,A,L) = \bar{u} \int_0^\infty S_{nn'}(x,T,A,L) x \, e^{-x} \, dx \tag{5}$$

The variable of integration x is the dimensionless collision energy E/kT and the factor $\bar{u}$ is the root mean square velocity. The dependence of cross section on E is transformed to the dependence on x and T for the purpose of integrating over all x, so the rate coefficient appears as a function of temperature T as well as the potential parameters A and L. In the more general case, the potential could be a function with as many parameters as desired, of course.

Finally, if the molecules are assumed to be harmonic oscillators, the relaxation time is very simply related to the rate coefficient (ref. 20)

$$\tau(T,A,L) = \frac{1}{n\alpha_{10}[1 - \exp(-\hbar\omega/kT)]} \tag{6}$$

where n is the molecule number density.

With this introduction to the steps to be followed, we are now prepared to discuss the semiclassical model of vibrational excitation in more detail.

SEMICLASSICAL TRANSITION RATE MODEL

Quantum Perturbation Theory

A brief review of the quantum mechanical perturbation method for calculating transition rates will be helpful for the purpose of discussing the perturbation potentials. The method begins by expressing the wave function Ψ of the system during collision as a linear superposition of the orthonormal set of wave functions ψ_n that describe the system in its unperturbed states

$$\Psi(q,t) = \sum_n a_n(t)\psi_n(q) e^{-iE_n t/\hbar} \tag{7}$$

The generalized coordinate q is understood to represent all the space coordinates involved in the problem, and E_n is the energy of the nth quantum state of the unperturbed system. If the total wave function is normalized, the squares of the absolute values of the coefficients $a_n(t)$ can be interpreted as the probability that the system will be in the state n at the time t. Thus, these squares sum to unity.

$$\sum_n \left| a_n^2(t) \right| = 1 \tag{8}$$

The wave function of equation (7) is introduced into Schroedinger's time dependent equation

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{9}$$

in which the Hamiltonian operator H is expressed as the sum of the Hamiltonian for the unperturbed system H^O (which is independent of time) and the perturbation energy U created by collision (which is a function of both molecular coordinates and time)

$$H = H^O(q) + U(q,t) \tag{10}$$

When both sides of equation (9) are multiplied by the complex conjugate wave functions ψ_n^*, $\exp(iE_{n'}t/\hbar)$ and integrated over all space, the differential equations for the coefficients $a_{n'}$ are obtained

$$\dot{a}_{n'} = -\frac{i}{\hbar} \sum_n a_n(t) H_{nn'}(t) e^{i\omega_{nn'}t} \qquad \text{for } n' = 1,2,3, \ldots \tag{11}$$

where the circular frequency is

$$\omega_{nn'} = \frac{E_{n'} - E_n}{\hbar} \tag{12}$$

and the transition matrix element $H_{nn'}$ is

$$H_{nn'}(t) = \left\langle \psi_{n'}^*(q) \middle| U(q,t) \middle| \psi_n(q) \right\rangle \tag{13}$$

Equations (11) are a coupled set that must be solved simultaneously for all the coefficients a_n, subject to the given initial conditions at $t = -\infty$. In the present case, the molecule is known to be in the state n before collision, so the initial conditions are

$$a_{n'}(-\infty) = \delta_{n'n} \begin{cases} 1 & \text{if } n' = n \\ 0 & \text{if } n' \neq n \end{cases} \tag{14}$$

The final values $\left| a_{n'}(+\infty) \right|^2$ represent the probability that the collision has caused transition to the state n'.

In some cases the deviation from the initial state is small throughout the collision. Then the differential equations for the coefficients $a_{n'}$ are uncoupled and become

$$\dot{a}_{n'} = - \frac{i}{\hbar} H_{nn'}(t) e^{i\omega_{nn'}t} \tag{15}$$

The transition rate $P_{nn'}$ is

$$P_{nn'} = |a_{n'}(+\infty)|^2 = \left| \frac{1}{\hbar} \int_{-\infty}^{\infty} H_{nn'}(t) e^{i\omega_{nn'}t} dt \right|^2 \tag{16}$$

The quantity $P_{nn'}$ can be interpreted as a transition probability only if it is small compared to unity. This will normally be the case at the relatively low collision energies which obtain when $kT \ll \hbar\omega_{nn'}$. In fact, over the range of temperatures where measured relaxation times are available for comparison with theory, $P_{nn'}$ is usually less than unity, even where kT is somewhat larger than $\hbar\omega$. However, at very high temperatures, $P_{nn'}$ can exceed unity and cannot then be identified as a probability. Physically, it represents a transition rate between states in the coupled set of equations (11). In principle, the coupling can be taken into account for strongly perturbed harmonic oscillator transitions, by an approximate method developed by Kerner (ref. 24), which yields transition probabilities as a function of P_{01}. Thus, calculation of P_{01} is the first step in the solution of the problem in either case - weak or strong coupling.

The matrix element $H_{nn'}$ needed for the calculation of $P_{nn'}$ is obtained from equation (13) once the perturbation energy $U(q,t)$ is defined. An approximation to this perturbation energy for homonuclear, diatomic molecules is developed in the next section.

<center>Approximate Perturbation Energy for Homonuclear
Diatomic Molecules</center>

The coordinate notation used to analyze the three-dimensional collision between a homonuclear, diatomic molecule and an inert collision partner is shown in figure 1. The center of the diatomic molecule is the origin (only one atom of the molecule is shown in figure 1; the second atom is understood to be symmetrically placed about the origin). The trajectory of relative motion between the particles is assumed to be determined by the spherically symmetric part of the interaction potential, in which case the trajectory (shown by the dashed curve) lies in a single plane (the x-y plane of fig. 1). The point of closest approach is taken to be on the x-axis a distance σ from the origin. The distances between the inert particle and the center of the molecule, the center of atom 1, and the center of atom 2 are designated by r, r_1, and r_2, respectively. The angle between the x-axis and the vector $\vec{r}$ is χ. The distance between atoms 1 and 2 is ρ, and the orientation of the molecular axis is defined by the polar angle θ from the z-axis and the
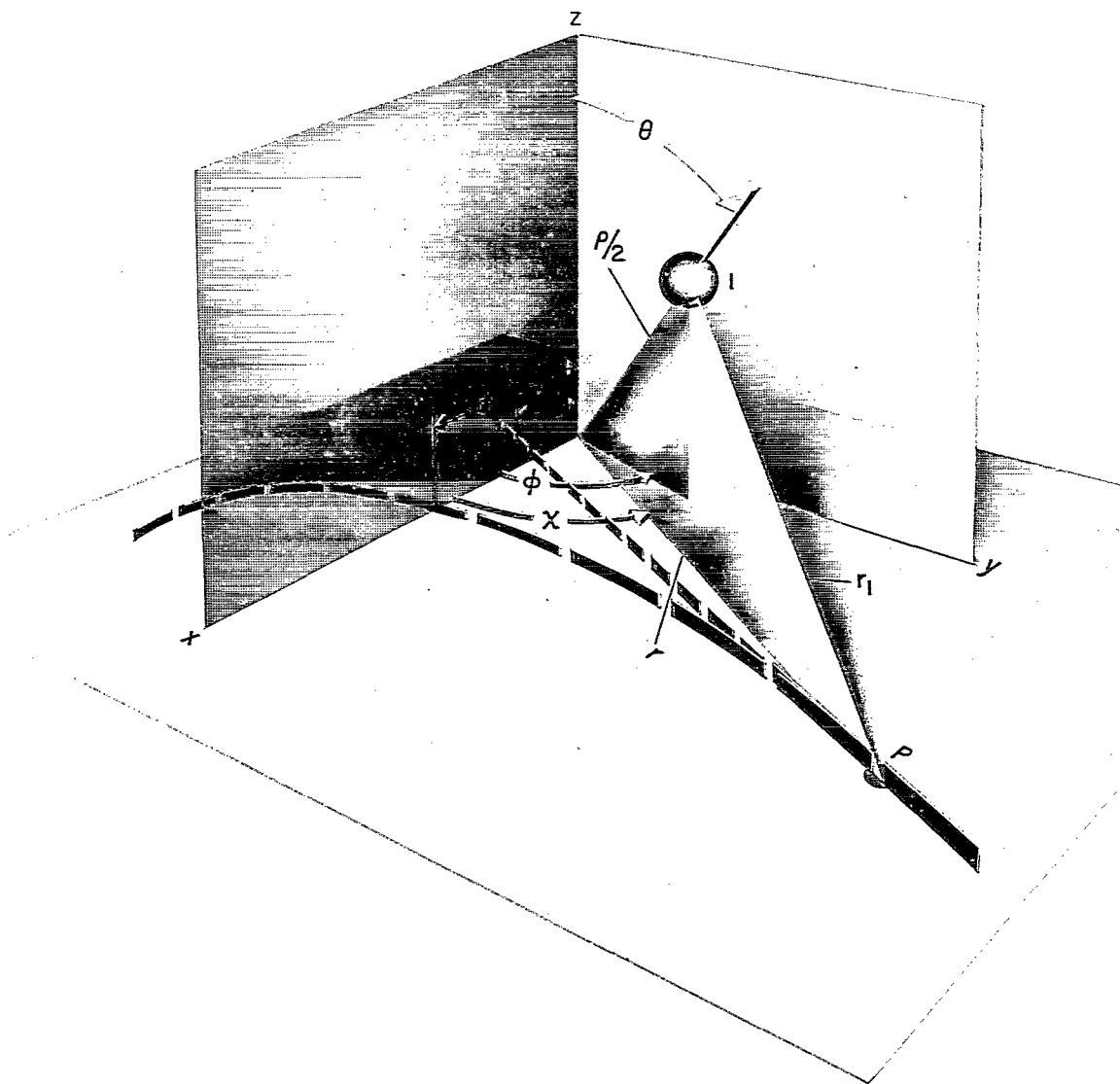
Figure 1.- Diagram showing collision coordinates.

azimuthal angle ϕ from the x-axis. Then the distances r_1 and r_2 are

$$r_1{}^2 = r^2\left[1 - \frac{\rho}{r}\sin\theta\cos(\phi - \chi) + \left(\frac{\rho}{2r}\right)^2\right] \tag{17a}$$

$$r_2{}^2 = r^2\left[1 + \frac{\rho}{r}\sin\theta\cos(\phi - \chi) + \left(\frac{\rho}{2r}\right)^2\right] \tag{17b}$$

8

Collisions are assumed to be weak enough that $(\rho/r) < 1$ for all r. Then, reasonable approximations for the distances r_1 and r_2 are

$$r_1 \simeq r - \frac{\rho}{2} \sin \theta \cos(\phi - \chi) \tag{18a}$$

$$r_2 \simeq r + \frac{\rho}{2} \sin \theta \cos(\phi - \chi) \tag{18b}$$

At this point the perturbation potential is taken to be a linear super-position of exponential repulsions, as in equation (1)

$$U = A\left(e^{-r_1/L} + e^{-r_2/L}\right) \simeq 2Ae^{-r/L} \cosh\left[\frac{\rho}{2L} \sin \theta \cos(\phi - \chi)\right] \tag{19}$$

The bond length ρ is very nearly equal to its equilibrium value ρ_e, and the angle χ is small in the region where the perturbation contributes appreciably to the Fourier transform. Accordingly, the perturbation is expanded to terms of first order in $\rho - \rho_e$ and χ

$$\frac{\rho}{2L} \sin \theta \cos(\phi - \chi) \simeq \frac{\rho_e}{2L} \sin \theta \cos \phi + \chi \frac{\rho_e}{2L} \sin \theta \sin \phi + \frac{\rho - \rho_e}{2L} \sin \theta \cos \phi \tag{20}$$

Then, if $\delta = \rho_e/2L$

$$U \simeq 2Ae^{-r/L}\Big[\cosh(\delta \sin \theta \cos \phi) + \chi\delta \sin \theta \sin \phi \sinh(\delta \sin \theta \cos \phi)$$

$$+ \frac{\rho - \rho_e}{2L} \sin \theta \cos \phi \sinh(\delta \sin \theta \cos \phi)\Big] \tag{21}$$

The spherically symmetric potential used to determine the collision trajectory is obtained by averaging over all configurations. The last two terms vanish because of asymmetry in ϕ and $(\rho - \rho_e)$, and the part remaining is

$$\overline{U} = 2Ae^{-r/L} \, \overline{\cosh(\delta \sin \theta \cos \phi)} = 2Ae^{-r/L} \frac{\sinh \delta}{\delta} \tag{22}$$

This spherical averaging procedure is common practice in quantum treatments, and often seems justified by the results. It is also justified in classical treatments of the motion when $\sigma \gg \rho$. Although σ may not exceed ρ by a large margin, the inequality $\sigma > \rho$ is usually satisfied at least, so the error in the approximation of spherical symmetry does not grow unreasonably large.

The constant $\overline{A}$ will be defined as

$$\overline{A} = 2A \frac{\sinh \delta}{\delta} \qquad (23)$$

This constant represents the effective potential size parameter for the total spherically symmetric potential when the effects of the two separate atoms in the molecule are added. The perturbation is now expressed as

$$U = \overline{U}_0 e^{-[(r-\sigma)/L]} \frac{\delta}{\sinh \delta} \left[\cosh(\delta \sin \theta \cos \phi) + \chi\delta \sin \theta \sin \phi \sinh(\delta \sin \theta \cos \phi) \right.$$

$$\left. + \frac{\rho - \rho_e}{2L} \sin \theta \cos \phi \sinh(\delta \sin \theta \cos \phi) \right] \qquad (24)$$

where $\overline{U}_0 = \overline{A} e^{-\sigma/L}$, the spherically averaged potential at the point of closest approach.

The first two terms in equation (24) are functions of only the rotational coordinates and are responsible for elastic scattering ($\Delta l = 0$) and pure rotational transitions ($\Delta l \neq 0$). The third term is linear in ($\rho - \rho_e$) and leads to vibrational transitions as well, which in the harmonic-oscillator, small-perturbation approximation consist of single vibrational quantum jumps ($\Delta v = \pm 1$). However, the appearance of the factor $\sin \theta \cos \phi \sinh(\delta \sin \theta \cos \phi)$ in this term means that these vibrational transitions can be accompanied by simultaneous rotational transitions, a feature missing from the one-dimensional collision model.

As far as vibrational transitions are concerned, the effective perturbation is just the third term, which may be expressed as

$$U = \frac{\overline{U}_0 e^{-[(r-\sigma)/L]}}{\sinh \delta} \left(\frac{\rho - \rho_e}{2L} \right) \sum_{n=1}^{\infty} \frac{(\delta \sin \theta \cos \phi)^{2n}}{(2n-1)!} \qquad (25)$$

From the symmetry of the angular coordinates, rotational transitions are limited to an even number of quantum jumps. Thus, the symmetry of the diatomic molecule's rotational wave function is preserved in these transitions, consistent with the expectation that collision perturbations are not likely to change nuclear spin. If nuclear spin is unchanged, rotational symmetry must be preserved to maintain antisymmetry of the total wave function.

The summation of equation (25) is uniformly convergent, even though δ is normally greater than unity. For typical values $\rho_e = 1$ Å and $L = 0.2$ Å, δ is about 2.5. Then the first two terms of the perturbation are about equal in mangitude, but the third term is only 15 percent as large as the first two, while the fourth term is only 2 percent as large and succeeding terms become very small. In view of these magnitudes, it is obviously necessary to carry at least the first two terms of the expansion; to simplify the

10

analysis we shall truncate the perturbation at this point, however.

$$U = \bar{U}_o e^{-[(r-\sigma)/L]} \frac{\delta^2}{\sinh \delta} \left(\frac{\rho-\rho_e}{2L}\right)\left(\sin^2 \theta \cos^2 \phi + \frac{\delta^2}{6} \sin^4 \theta \cos^4 \phi\right) \qquad (26)$$

In this case, the coupled rotational transitions are limited to $\Delta l = 0$, ± 2, ± 4. The various overlap integrals and the matrix elements resulting from the perturbation of equation (26) are worked out in appendix A. The truncation does not seriously affect the value of $\sinh \delta$, so this factor is retained without change.

The factor $\exp[-(r-\sigma)/L]$ contains the functional dependence on time which determines the magnitude of the Fourier transforms in equation (16). The classical equations of motion will next be used to develop an approximation for this time-dependent factor.

Classical Trajectory Impulse Functions

The classical trajectory for a spherically symmetric potential lies in a single plane as shown in figure 2 (the x-y plane of fig. 1). The velocity of relative motion at large r is u, and the impact parameter b is the initial miss distance. Energy and angular momentum changes involved in the internal state transitions of the diatomic molecule will be neglected compared with the kinetic energy and angular momentum of the collision partners, so that the latter can be treated as conserved quantities. (Later some adjustments will be made to account for conservation of total energy.) Conservation of the angular momentum of the collision partners requires that
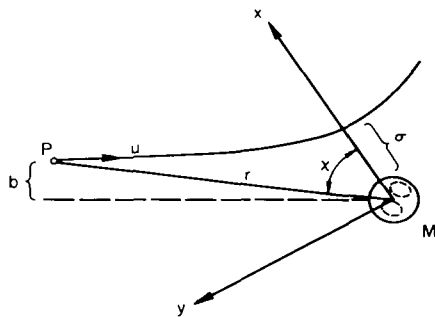
Figure 2.- Classical trajectory of relative motion between particle P and molecule M.

$$mr^2\dot{\chi} = mub \qquad (27)$$

while conservation of energy requires that

$$\frac{m}{2}(\dot{r}^2 + r^2\dot{\chi}^2) + \bar{U}(r) = \frac{mu^2}{2} \qquad (28)$$

where m is the reduced mass of the two collision partners and $\bar{U}(r)$ is the spherically symmetric average potential obtained in equation (22). Solving for $\dot{\chi}$ from equation (27) and substituting in equation (28), one obtains

$$|\dot{r}| = u\left[1 - \frac{2\overline{U}(r)}{mu^2} - \frac{b^2}{r^2}\right]^{1/2} \tag{29}$$

At the distance of closest approach $\dot{r}$ vanishes by symmetry (for an elastic collision) and from equation (29)

$$b^2 = \sigma^2\left(1 - \frac{2\overline{U}_\sigma}{mu^2}\right) \tag{30}$$

Precise knowledge of the potential is most important near the turning point where the perturbation is largest. Expansions about the point of closest approach ($t = 0$) yield the even function for the perturbation impulse $\overline{U}(t)$

$$\overline{U}(t) = \overline{U}_0 e^{-[(r-\sigma)/L]} \simeq \overline{U}_0 e^{-[(\ddot{r}_0 t^2/2L)+(r_0^{iv}t^4/24L)+\,.\,.\,.]} \tag{31}$$

and the odd function for the angle $\chi(t)$

$$\chi(t) = \dot{\chi}_0 t + \dddot{\chi}_0 \frac{t^3}{6} + \,.\,.\,. \tag{32}$$

All time derivatives at the turning point may be evaluated in terms of L, b, and σ (i.e., r_0)

$$\left.\begin{aligned}
\ddot{r}_0 &= \frac{\overline{U}_0}{mL} + \frac{u^2b^2}{\sigma^3}\\[2mm]
r_0^{iv} &= -\left(\frac{\overline{U}_0}{mL^2} + \frac{3u^2b^2}{\sigma^4}\right)\ddot{r}_0
\end{aligned}\right\} \tag{33}$$

$$\left.\begin{aligned}
\dot{\chi}_0 &= \frac{ub}{\sigma^2}\\[2mm]
\dddot{\chi}_0 &= -\frac{2u^3b^3}{\sigma^6}\left(1 + \frac{\overline{U}_0\sigma^3}{mu^2Lb^2}\right)
\end{aligned}\right\} \tag{34}$$

For most purposes it would be sufficient to use just the first term in the expansion for χ, but, as we have seen, this quantity is not needed for calculations of vibrational transitions anyway. Only the exponential function in equation (31) is needed for this purpose, and this function is very sensitive to the exact value of r. The first exponential factor falls too rapidly as t^2 increases. The following factors oscillate in sign of the exponent, and the total expression does not converge very rapidly. Thus equation (31)

is not very useful as it stands. However, for the exponential potential form an exact solution does exist for head-on collisions (refs. 12, 13, 19) ($b = 0$, $\overline{U}_O = mu^2/2$)

$$\overline{U}(t) = \overline{U}_O \operatorname{sech}^2(at) \tag{35}$$

The constant a is $u/2L$ when $b = 0$. Now it is anticipated that the most effective collisions are those where the miss distance is small, since these penetrate deepest into the potential and cause the strongest perturbations. Therefore, we choose a solution with the same form as equation (35) that will reduce to the exact solution when $b = 0$, but let the constant a take the value that gives the correct first-order terms in the expansion of the three-dimensional trajectory about the point of closest approach

$$a^2 = \frac{\ddot{r}_O}{2L} = \frac{1}{2L}\left(\frac{\overline{U}_O}{mL} + \frac{u^2 b^2}{\sigma^3}\right) \tag{36}$$

We shall define ε as the fraction of the collision kinetic energy that is transformed into potential energy at the point of closest approach

$$\varepsilon = \frac{2\overline{U}_O}{mu^2} = \frac{\overline{U}_O}{E} \tag{37}$$

In terms of ε, the constant a may be expressed

$$a^2 = \left(\frac{u}{2L}\right)^2 \left[1 - (1 - \varepsilon)\left(1 - \frac{2L}{\sigma}\right)\right] \tag{38}$$

This value of a gives the correct form near the turning point at the expense of some mismatch in the asymptotic behavior. The particles should recede from one another with a velocity u at very large time, while the asymptotic form of equation (35)

$$\overline{U}(t) \xrightarrow[t\to\infty]{} 4\overline{U}_O e^{-2at} = 4\varepsilon \left(\frac{mu^2}{2}\right) e^{-(ut/L)\{1-(1-\varepsilon)[1-(2L/\sigma)]\}^{1/2}} \tag{39}$$

corresponds to an escape velocity $u\{1 - (1 - \varepsilon)[1 - (2L/\sigma)]\}^{1/2}$. Even so, equation (35) is a far better approximation than the simple expansion of equation (31), for the asymptotic behavior is correctly described as $\varepsilon \to 1$. Actually, we need not be particularly concerned with the slowly varying perturbation far from the turning point, since this portion does not contribute appreciably to the Fourier transform in equation (16). Rather, an approximation is required which is nearly correct in the region where the rate of change dU/dt has passed its maximum, as this will pick up the major contribution to the Fourier transform. Equation (35) should be a reasonable approximation in this sense as long as $\varepsilon \simeq 1$, and this may be sufficient to pick up the important contribution to the vibrational transition cross section.

The perturbation potential of equation (26) is next used to calculate the transition probabilities, the cross sections, and the rate coefficients for vibrational transitions produced by low energy collisions, where the small perturbation method is valid. These calculations will illustrate the procedures outlined in the General Discussion of the Problem.

TRANSITION PROBABILITIES, CROSS SECTIONS, AND RATE COEFFICIENTS

Vibrational Transition Probability

That part of the perturbation function which contributes to vibrational transition has been approximated

$$U = \varepsilon\left(\frac{mu^2}{2}\right) \text{sech}^2(at) \frac{\delta^2}{\sinh \delta} \left(\frac{\rho-\rho e}{2L}\right)\left(\sin^2 \theta \cos^2 \phi + \frac{\delta^2}{6} \sin^4 \theta \cos^4 \phi\right) \tag{40}$$

The perturbation matrix element for simultaneous transition from quantum state (v, l, m) to state (v', l', m') is

$$H(v,l,m;v',l',m') = \beta(v,l,m;v',l',m')\varepsilon\left(\frac{mu^2}{2}\right) \text{sech}^2(at) \tag{41}$$

where the constant $\beta(v, l, m; v', l', m')$ is the overlap integral

$$\beta(v,l,m;v',l',m') = \left\langle \psi^*_{v'l'm'} \left| \frac{\delta^2}{\sinh \delta} \left(\frac{\rho-\rho e}{2L}\right)\left(\sin^2 \theta \cos^2 \phi + \frac{\delta^2}{6}\sin^4 \theta \cos^4 \phi\right) \right| \psi_{vlm} \right\rangle \tag{42}$$

These constants are evaluated in appendix A for the usual rigid-rotator, harmonic-oscillator wave functions. Changes in vibrational quantum number are limited to $\Delta v = \pm 1$, while changes in rotational quantum number are limited to $\Delta l = 0, \pm 2, \pm 4$. The changes in magnetic quantum number are limited to $\Delta m = 0, \pm 2, \pm 4$ also, and these correspond to reorientation of the angular momentum vector in space as result of the collision. The energy of the rigid rotator does not depend on magnetic quantum number, so the transitions involving different initial values of m can be averaged to obtain a total transition probability for $(v, l) \rightarrow (v', l')$. Since the probability is proportional to the matrix element squared, the values of β^2 must be averaged to get the total matrix element squared for a given transition (v, l) to $(v+\Delta v, l+\Delta l)$.

$$\beta^2(\Delta v, \Delta l) = \sum_{\Delta m=0,\pm 2,\pm 4} \left[\frac{1}{2l+1} \sum_m \beta^2(v,l,m;v+\Delta v,l+\Delta l,m+\Delta m)\right] \tag{43}$$

All of the transitions involved in this average have the same value of circular frequency

$$\omega = \omega(\Delta v, \Delta l) = \left| \frac{E_{v'l'} - E_{vl}}{\hbar} \right| \tag{44}$$

Although it is difficult to average over m in general, the average approaches a simple limiting value for $l \gg 1$, as shown in appendix A. This limit will be used here, inasmuch as l is the order of 10 or greater for most of the collisions that occur in gases at the temperatures of interest, $kT \approx \hbar\omega$. Furthermore, the limiting average for large l is independent of l, which is fortunate in view of the averaging over a Boltzmann distribution of rotational states that must be performed eventually.

According to the results in appendix A, the final values for the averaged matrix elements squared are

$$\beta^2(\pm 1, 0) = \left(\frac{2}{15} + \frac{\delta^2}{35} + \frac{\delta^4}{630} \right) \left(\frac{\delta^4}{\sinh^2 \delta} \right) \left[\frac{v + (1/2) \pm (1/2)}{8L^2 \mu\omega/\hbar} \right] \tag{45a}$$

$$\beta^2(\pm 1, \pm 2) = \left(\frac{1}{30} + \frac{\delta^2}{105} + \frac{2\delta^4}{2835} \right) \left(\frac{\delta^4}{\sinh^2 \delta} \right) \left[\frac{v + (1/2) \pm (1/2)}{8L^2 \mu\omega/\hbar} \right] \tag{45b}$$

$$\beta^2(\pm 1, \pm 4) = \left(\frac{\delta^4}{22680} \right) \left(\frac{\delta^4}{\sinh^2 \delta} \right) \left[\frac{v + (1/2) \pm (1/2)}{8L^2 \mu\omega/\hbar} \right] \tag{45c}$$

where μ is the reduced mass of the diatomic molecule. The next term in the expansion of the perturbation function of equation (25) will contribute something to the terms of order δ^6, but not to the lower order terms.

Note that diatomic molecules with electronic states other than $^1\Sigma$ should, strictly speaking, be described by symmetric top wave functions. However, the projection of electronic spin and angular momenta on the internuclear axis is rarely more than 3/2 quantum units in molecules of interest, so at high rotational quantum numbers l, the perturbation of rigid-rotator wave functions by electronic momentum should be small. Accordingly, we apply the above rigid-rotator matrix elements to diatomic molecules in general.

The Fourier transform of the $\text{sech}^2(at)$ is a well-known integral

$$\int_{-\infty}^{\infty} (\text{sech}^2 at) e^{i\omega t} dt = \frac{\pi\omega}{a^2} \text{csch} \frac{\pi\omega}{2a} \xrightarrow[(\omega/a) \gg 1]{} \frac{2\pi\omega}{a^2} e^{-(\pi\omega/2a)} \tag{46}$$

Thus, in the limit as $(\omega/a) \gg 1$, which is a condition for small perturbation theory to be valid, the transition probability becomes

$$P = \left[\beta \frac{\varepsilon}{\hbar} \left(\frac{mu^2}{2} \right) \frac{2\pi\omega}{a^2} \right]^2 e^{-(\pi\omega/a)} \tag{47}$$

15

where the indices indicating the particular transition involved are dropped for economy in notation. The terms P, ω, and β are understood to represent the values of $P(\Delta v, \Delta l)$, $\omega(\Delta v, \Delta l)$, and $\beta(\Delta v, \Delta l)$. The latter two constants are given by equations (44) and (45), respectively.

Vibrational Transition Cross Section

The collision cross section for the transition may be expressed

$$S = P_o \int_o^\infty \frac{P}{P_o} \, 2\pi b \, db \tag{48}$$

where P_o represents the transition rate for head-on collisions when $b = 0$. According to equation (47)

$$\frac{P}{P_o} = \epsilon^2 \left(\frac{a_o}{a}\right)^4 e^{-(\pi\omega/a_o)[(a_o/a)-1]} \tag{49}$$

and from equation (39)

$$\frac{a_o}{a} = \left[1 - (1 - \epsilon)\left(1 - \frac{2L}{\sigma}\right)\right]^{-1/2} \tag{50}$$

where $a_o = u/2L$, σ is the distance of closest approach, and σ_o will be used to designate that particular value of σ which occurs for head-on collisions, that is, when $b = 0$. From the relation between b and σ (see eq. (30))

$$b^2 = \sigma^2(1 - \epsilon) \tag{51}$$

it follows that

$$2\pi b \, db = -\pi\sigma^2\left[1 - \frac{2(1-\epsilon)}{\sigma} \frac{d\sigma}{d\epsilon}\right] d\epsilon \tag{52}$$

For the exponential form of the interaction potential assumed here

$$\epsilon = e^{-[(\sigma-\sigma_o)/L]}, \qquad \frac{d\sigma}{d\epsilon} = -\frac{L}{\epsilon} \tag{53}$$

and in this case, equation (52) becomes

$$2\pi b \, db = -\pi\sigma^2\left(1 + \frac{2L}{\sigma}\frac{1-\epsilon}{\epsilon}\right) d\epsilon \tag{54}$$

16

Substituting equations (50) and (54) into the pre-exponential factor of the integrand in equation (48), one obtains

$$S = P_o \int_o^1 \frac{\pi\sigma^2}{1 + \frac{2L}{\sigma}\left(\frac{1-\epsilon}{\epsilon}\right)} e^{-(\pi\omega/a_o)[(a_o/a)-1]} \, d\epsilon \tag{55}$$

It can be anticipated that if $\pi\omega/a_o \gg 1$, the major contribution to this integral will come from the region where $\epsilon \simeq 1$ and $a \simeq a_o$. Therefore, the integrand of equation (55) will be expanded to terms of first order in $(1 - \epsilon)$. From equation (53)

$$\sigma = \sigma_o\left(1 - \frac{L}{\sigma_o}\ln\epsilon\right) = \sigma_o\left[1 + \frac{L}{\sigma_o}(1 - \epsilon) + \ldots\right] \tag{56}$$

Thus

$$\frac{\pi\sigma^2}{1 + \frac{2L}{\sigma}\left(\frac{1-\epsilon}{\epsilon}\right)} = \frac{\pi\sigma_o^2\left[1 + \frac{2L}{\sigma_o}(1 - \epsilon) + \ldots\right]}{\left[1 + \frac{2L}{\sigma_o}(1 - \epsilon) + \ldots\right]} \simeq \pi\sigma_o^2 \tag{57}$$

while from equation (50)

$$\frac{a_o}{a} - 1 \simeq \frac{1}{2}\left(1 - \frac{2L}{\sigma_o}\right)(1 - \epsilon) \tag{58}$$

Thus, to this approximation, the cross section becomes

$$S = \pi\sigma_o^2 P_o \int_o^1 e^{-(\pi\omega/2a_o)[1-(2L/\sigma_o)](1-\epsilon)} \, d\epsilon \tag{59}$$

This integration is easily performed to give

$$S = \frac{\pi\sigma_o P_o}{\left(\frac{\pi\omega}{2a_o}\right)\left(1 - \frac{2L}{\sigma_o}\right)}\left\{1 - e^{-(\pi\omega/2a_o)[1-(2L/\sigma_o)]}\right\} \tag{60}$$

In the limit as $(\pi\omega/2a_o) \gg 1$, the cross section takes the form

$$S = \frac{\pi\sigma_o^2}{\left(\frac{\pi\omega}{2a_o}\right)\left(1 - \frac{2L}{\sigma_o}\right)}P_o = \frac{\pi\sigma_o^2}{1 - \frac{2L}{\sigma_o}}\left(\frac{2\beta mu^2}{\hbar a_o}\right)^2\left(\frac{\pi\omega}{2a_o}\right)e^{-(\pi\omega/a_o)} \tag{61}$$

The factor $\pi\sigma_o^2/(\pi\omega/2a_o)[1 - (2L/\sigma_o)]$ may be thought of as the effective total cross section for vibrational transition to be used with the one-dimensional collision transition probability P_o. It can be seen that this steric factor is not constant, as usually assumed, but because of the three-dimensional nature of the collision, is approximately proportional to the velocity, u, as suggested by Calvert and Amme (ref. 27).

In the other limit as $\pi\omega/2a_o[1 - (2L/\sigma_o)] \ll 1$, the effective cross section approaches $\pi\sigma_o^2$, according to equation (60). This is a physically plausible result, though the assumptions made tend to break down in this limit.

Vibrational Transition Rate Coefficients

The cross section is next averaged over a Boltzmann distribution of collision energies to get the rate coefficient α

$$\alpha = \frac{\bar{u}}{s} \int_o^\infty Sxe^{-x} \, dx \tag{62}$$

where x is the dimensionless collision energy $mu^2/(2kT)$, m is the reduced mass of the collision partners, and $\bar{u}$ is the mean velocity $(8kT/\pi m)^{1/2}$. The symmetry number (s) is unity for collisions between unlike molecules, but must be 2 for collisions between like molecules, in order to avoid counting collision systems twice in this case.

Some allowance must now be made to account for conservation of energy in those collisions that cause vibrational transition. Rapp (ref. 19) lets the effective collision velocity u be the average of initial and final velocities $(u_i + u_f)/2$, and Herzfeld (ref. 20) points out that this substitution is necessary to reconcile the classical and quantum results. To terms of second order this is equivalent to letting the effective collision energy be the average of the initial and final energies.

$$\frac{mu^2}{2} = \frac{mu_i^2}{2} \pm \frac{\hbar\omega}{2} \tag{63}$$

where u_i is the initial velocity. The use of the $\pm$ sign depends on whether the transition is to the adjacent lower or upper vibrational state, respectively. The effective dimensionless collision energy x is, accordingly

$$x = x_i \pm \frac{\hbar\omega}{2kT} \tag{64}$$

where x_i is $mu_i^2/2kT$, the initial value of x. The cross section has been derived as a function of x, while the Boltzmann distribution of collision energies given in equation (62) is really a function of x_i, the initial value. The variable of integration is changed from x_i to x, and the rate coefficient becomes

18

$$\alpha = \frac{\overline{u}}{s} e^{\pm(\hbar\omega/2kT)} \int_{\hbar\omega/2kT}^{\infty} S(x)\left(x \mp \frac{\hbar\omega}{2kT}\right) e^{-x} dx \qquad (65)$$

The factor $\exp(\pm\hbar\omega/2kT)$ is exactly that required so that the ratio of the forward rate to the reverse rate is the Arrhenius factor $\exp(-\hbar\omega/kT)$, which preserves detailed balancing at equilibrium. The lower limit of the integral is found to be the same for either excitation or deexcitation, since the excitation cross section vanishes for collision energies less than $\hbar\omega$.

The cross section has been found as a function of the effective velocity u in equation (61)

$$S = \left(\frac{\pi\sigma_0^2}{1 - \frac{2L}{\sigma_0}}\right) \frac{16\pi\beta^2 m^2 \omega L^3 u}{\hbar^2} e^{-(2\pi\omega L/u)} \qquad (66)$$

It will be convenient to express this result in terms of the dimensionless collision energy x and a characteristic energy E_c

$$E_c = \frac{m\omega^2 L^2}{2} \qquad (67)$$

Then equation (66) becomes

$$S = \left(\frac{\pi\sigma_0^2}{1 - \frac{2L}{\sigma_0}}\right) F x^{1/2} e^{-(G/x^{1/2})} \qquad (68)$$

where the constants F and G are

$$F = 64\pi\beta^2 \left(\frac{E_c^3 kT}{\hbar^4\omega^4}\right)^{1/2} \qquad (69)$$

$$G = 2\pi \left(\frac{E_c}{kT}\right)^{1/2} \qquad (70)$$

Substituting equation (68) into (65), one obtains for the rate coefficient

$$\alpha = \frac{\overline{u}F}{s} e^{\pm(\hbar\omega/2kT)} \int_{\hbar\omega/2kT}^{\infty} \frac{\pi\sigma_0^2}{1 - \frac{2L}{\sigma_0}} x^{1/2}\left(x - \frac{\hbar\omega}{2kT}\right) e^{-[x+(G/x^{1/2})]} dx \qquad (71)$$

The integrand has a sharp maximum primarily determined by the factor
$\exp-[x - (G/x^{1/2})]$. This factor has its maximum where the exponent is a
maximum,

$$x_m = \left(\frac{G}{2}\right)^{2/3} = \left(\frac{\pi^2 E_c}{kT}\right)^{1/3} \tag{72}$$

The characteristic energy E_c is several eV for most diatomic molecules,
and the constant G is the order of 10 to 100; therefore, the maximum occurs
at rather large values of x, just as we assumed when the corrections to the
pre-exponential factors and to the lower limit of the rate coefficient integral
were ignored.

The pre-exponential factors $x^{1/2}[x - (\hbar\omega/2kT)]$ and σ_0 in equation (71)
are evaluated at x_m, and the exponent is expanded about x_m

$$x_m^{1/2}\left(x_m - \frac{\hbar\omega}{2kT}\right) \simeq x_m^{3/2} \tag{73}$$

$$x_m + \frac{G}{x^{1/2}} = 3x_m + \frac{3}{4x_m}(x - x_m)^2 + \ldots \tag{74}$$

$$\alpha = \frac{\bar{u}}{s}\left(\frac{\pi\sigma_0^2}{1 - \frac{2L}{\sigma_0}}\right)_m Fx_m^{3/2} e^{-3x_m \pm (\hbar\omega/2kT)} \int_{\hbar\omega/2kT}^{\infty} e^{-(3/4x_m)(x-x_m)^2} dx \tag{75}$$

The integral in equation (75) is approximately

$$\int_0^{\infty} e^{-3y^2/4x_m} dy \simeq \sqrt{\frac{4\pi x_m}{3}} \tag{76}$$

and the constant F expressed in terms of x_m is

$$F = \beta^2\left(\frac{8kT}{\pi\hbar\omega}\right)^2 x_m^{9/2} \tag{77}$$

so the rate coefficient finally becomes

$$\alpha = \frac{\beta^2}{s}\left(\frac{4\pi}{3}\right)^{1/2}\left(\frac{\pi\sigma_0^2}{1 - \frac{2L}{\sigma_0}}\right)_m \bar{u}\left(\frac{8kT}{\pi\hbar\omega}\right)^2 x_m^{13/2} e^{-3x_m \pm (\hbar\omega/2kT)} \tag{78}$$

where the distance of closest approach for head-on collisions at the energy $x_m kT$ is

$$\sigma_o = -L \, \ln \left(\frac{mu_m^2}{2\overline{A}} \right) = L \, \ln \left(\frac{\overline{A}}{x_m kT} \right) \tag{79}$$

The rate coefficient, expressed in terms of temperature and the characteristic energy E_c, is

$$\alpha = \frac{\beta^2}{s} \left(\frac{4\pi}{3} \right)^{1/2} \left(\frac{\pi \sigma_o^2}{1 - \frac{2L}{\sigma_o}} \right)_m \left(\frac{8kT}{\pi m} \right)^{1/2} \left(\frac{8\pi E_c}{\hbar \omega} \right)^2 \left(\frac{\pi^2 E_c}{kT} \right)^{1/6} e^{-3(\pi^2 E_c/kT)^{1/3} \pm \hbar \omega / 2kT} \tag{80}$$

where the total cross section at the velocity u_m is

$$\left(\frac{\pi \sigma_o^2}{1 - \frac{2L}{\sigma_o}} \right)_m = \frac{\frac{\pi L^2}{9} \left(\ln \frac{\overline{A}^3}{\pi^2 k^2 T^2 E_c} \right)^2}{1 - \frac{6}{\ln(\overline{A}^3/\pi^2 k^2 T^2 E_c)}} \tag{81}$$

Equation (80) demonstrates the familiar result (refs. 4, 11, 19) that $\ln \alpha$ varies essentially as $-T^{-1/3}$.

Rapp (ref. 19) called attention to one additional factor, due to long-range attractive forces in the intermolecular potential, which can become important at low temperature. If the depth of the potential well is Δ, the collision energy is effectively increased by Δ before it is absorbed in climbing the potential barrier. This amounts to a shift in the Boltzmann distribution of collision energies by the factor $\exp(\Delta/kT)$. Since this factor does not enter the integrations, it simply multiplies the final results of equations (78) and (80).

Equation (78) or (80) gives the rate coefficient for a specific vibration-rotation transition. The values of β^2 and ω will be different for different transitions; recall that the indices specifying the exact transition were omitted for convenience. Now, however, the total rate coefficient for a given vibrational transition, $\alpha(\Delta v)$, is obtained by summing the coefficients for all possible rotational transitions, $\alpha(\Delta v, \Delta l)$, and averaging over the initial distribution of rotational states

$$\alpha(\Delta v) = \sum_{\Delta l = 0, \pm 2, \pm 4} \overline{\alpha(\Delta v, \Delta l)} \tag{82}$$

This is accomplished by substituting for β^2 in equation (80) an appropriate weighted average, which is derived in the next section.

Effect of Rotational Excitation

To a first approximation, the energies and the circular frequencies $\omega(\Delta v, \Delta l)$ are independent of the rotational quantum number l. In the limit as $l \gg 1$, the matrix elements averaged over all values of m, $\beta^2(\Delta v, \Delta l)$, are also independent of l, as shown in appendix A. Thus, the final matrix element for a given vibrational transition Δv may simply be taken as the sum

$$\beta^2(\Delta v) = \sum_{\Delta l = 0, \pm 2, \pm 4} \beta^2(\Delta v, \Delta l) \tag{83}$$

and this value used in equation (80) will give the first-order approximation to the total rate coefficient for a given vibrational transition v to $v + \Delta v$.

In the second approximation, the small variations of ω are taken into account. To first order in v and l, the energy of a given state is

$$E = \hbar\omega\left(v + \frac{1}{2}\right) + Bl(l + 1) \tag{84}$$

where B is the rotational energy constant. The circular frequencies for the allowed transitions are

$$\omega(\Delta v, \Delta l) = \frac{E_{v+\Delta v, l+\Delta l} - E_{v, l}}{\hbar} = \omega\left[\Delta v + \frac{2B\Delta l}{\hbar\omega}\left(l + \frac{\Delta l + 1}{2}\right)\right] \tag{85}$$

Since l is normally large compared with unity, $[(\Delta l + 1)/2]$ will be neglected compared with l, and the approximate expression used for the circular frequency is

$$\omega(\Delta v, \Delta l) \approx \omega\left[\Delta v + \left(\frac{2B\Delta l}{\hbar\omega}\right)l\right] \tag{86}$$

Then, approximate corrections to the first-order rate coefficient $\alpha(\Delta v, 0)$ are

$$R(\Delta v, \Delta l) = \frac{\alpha(\Delta v, \Delta l)}{\alpha(\Delta v, 0)} = \left[\frac{\omega(\Delta v, \Delta l)}{\omega(\Delta v, 0)}\right]^{7/3} e^{-3x_m\left\{[\omega(\Delta v, \Delta l)/\omega(\Delta v, 0)]^{2/3} - 1\right\}} \tag{87}$$

Using equation (86), and setting $\omega(\Delta v, 0) = \omega_0$, it is found that

$$\frac{\omega(\Delta v, \Delta l)}{\omega_0} = 1 + \left(\frac{2B\Delta l}{\hbar\omega_0}\right)l$$

Since $(2B/\hbar\omega_0) \approx 2\times10^{-3}$ for typical molecules, the exponent in equation (87) may be expanded and

$$R(\Delta v, \Delta l) \approx \left[1 + \left(\frac{2B\Delta l}{\hbar\omega_0}\right) l\right]^{7/3} e^{-x_m(4B\Delta l/\hbar\omega_0)l} \tag{88}$$

Dependence of $R(\Delta v, \Delta l)$ on l is removed when the correction factor is averaged over a Boltzmann distribution of initial rotational quantum numbers

$$\overline{R(\Delta v, \Delta l)} = \frac{B}{kT} \sum_{l=0}^{\infty} R(\Delta v, \Delta l)(2l+1)e^{-(B/kT)l(l+1)} \tag{89}$$

An analytic approximation for this average can be obtained by replacing the summation with an integral. Set

$$\lambda = \frac{2B|\Delta l|}{\hbar\omega_0}\left(\frac{kT}{B}\right)^{1/2}$$

$$g = x_m\lambda$$

$$y^2 = \frac{B}{kT} l(l + 1)$$

$$l \approx y\left(\frac{kT}{B}\right)^{1/2}$$

Then

$$\overline{R(\Delta v, \Delta l)} = e^{g^2} \int_0^{\infty} (1 + \lambda y)^{7/3} e^{-(y+g)^2} 2y \, dy \qquad \left(\frac{\Delta l}{\Delta v} > 0\right) \tag{90a}$$

$$\overline{R(\Delta v, \Delta l)} = e^{g^2} \int_0^{\infty} (1 - \lambda y)^{7/3} e^{-(y-g)^2} 2y \, dy \qquad \left(\frac{\Delta l}{\Delta v} < 0\right) \tag{90b}$$

The integrand in equation (90a) has a maximum near $y = 0$ and in equation (90b) the integrand has a maximum near $y = g$. Using these values for y in the pre-exponential term, and integrating the resulting simplified integral gives

$$\overline{R(\Delta v, \Delta l)} = 1 - \sqrt{\pi} \, g \, e^{g^2}(1 - \text{erf}[g]) \qquad \left(\frac{\Delta l}{\Delta v} > 0\right) \tag{91a}$$

$$\overline{R(\Delta v, \Delta l)} = (1 - \lambda g)^{7/3}\left[1 + \sqrt{\pi} \, g \, e^{g^2}(1 + \text{erf}[g])\right] \qquad \left(\frac{\Delta l}{\Delta v} < 0\right) \tag{91b}$$

23

These are combined to give a total correction factor for a given $|\Delta l|$.

$$\overline{R(\Delta v, |\Delta l|)} = 1 - \sqrt{\pi}\ g\ e^{g^2}(1 - \text{erf}[g]) + (1 - \lambda g)^{7/3}\left[1 + \sqrt{\pi}\ g\ e^{g^2}(1 + \text{erf}[g])\right]$$
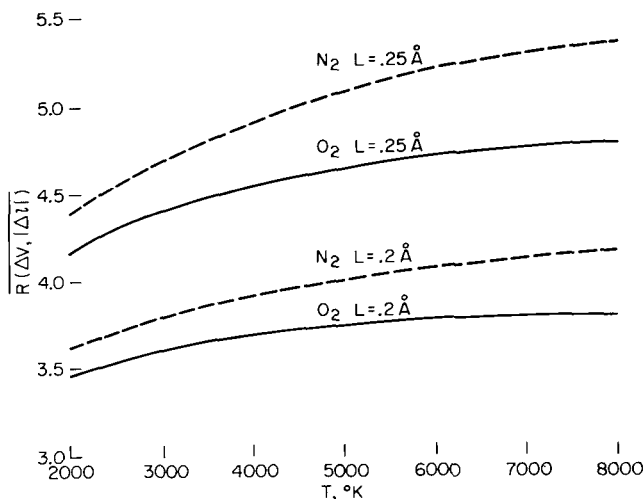
(92)

The correction factors given by equation (92) are shown as functions of temperature in figures 3 and 4 for diatomic molecules N_2 and O_2 and for typical values of L = 0.2 and 0.25 Å. It is seen that transitions $v \to v \pm 1$, $l \to \mp 2$ can increase in probability by factors of about 4 and that transitions $v \to v \pm 1$, $l \to l \mp 4$ can increase by factors of 10. The matrix elements β^2 depend only on the absolute magnitude of the change in l, so the total correction for a given change $|\Delta l|$ is the sum of equations (91a) and (91b). For all transitions involving a given change in vibrational quantum number Δv, the weighted average value to be used for β^2 in calculating the total rate coefficient is

$$\beta^2(\Delta v) = \sum_{\Delta l = 0, \pm 2, \pm 4} \overline{R(\Delta v, \Delta l)}\ \beta^2(\Delta v, \Delta l)$$

(93)

and

$$\frac{\alpha}{\alpha_0} = \frac{\displaystyle\sum_{\Delta l = 0, \pm 2, \pm 4} \overline{R(\Delta v, \Delta l)}\ \beta^2(\Delta v, \Delta l)}{\displaystyle\sum_{\Delta l = 0, \pm 2, \pm 4} \beta^2(\Delta v, \Delta l)}$$

(94)

This ratio is shown for O_2 and N_2 in figure 5 for L = 0.20 and 0.25 Å. The total transition rate is seen to increase by factors of 1.5 to 2 when coupled rotations are taken into account. Such an effect could simply be swallowed by the empirical cross-section factor in the one-dimensional

Figure 3.- Correction factor $\overline{R(\Delta v, |\Delta l|)}$ for $|\Delta l| = 2$ and L = 0.2 and L = 0.25.
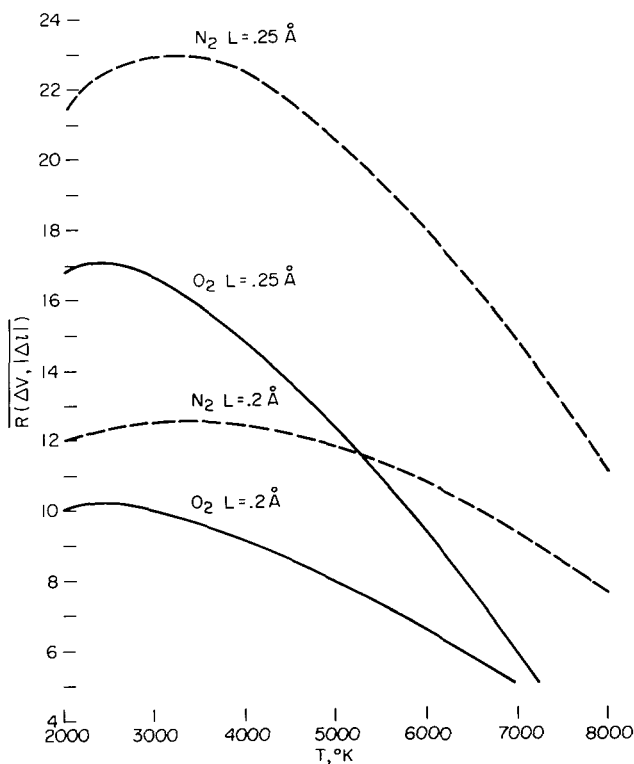
Figure 4.- Correction factor $\overline{R(\Delta v, |\Delta l|)}$ for $|\Delta l| = 4$ and L = 0.2 and L = 0.25.
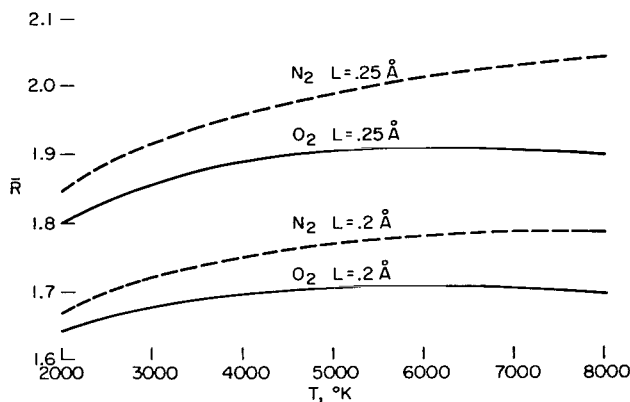
Figure 5.- Total rotational correction for the rate coefficient, $\bar{R} = (\alpha/\alpha_0)$.

collision model, of course, but in the absolute three-dimensional model a factor of this size makes some difference in the fit of theory to data.

It may be helpful to summarize here the essential formulas for the particular rate coefficient α_{10}, which is of primary interest. The potential parameters $\bar{A}$ and L, the reduced mass m, and the symmetry number s are all determined by the two collision partners involved; the circular frequency ω_0, the equilibrium interatomic distance ρ_e, the molecular reduced mass μ, and the rotational energy constant B are all characteristic of the diatomic molecule which is vibrationally de-excited. In terms of these parameters and the thermal energy kT, the rate coefficient for de-excitation from the first vibrational state is

$$\alpha_{10} = \frac{\beta_{10}^2}{s} \left(\frac{4\pi}{3}\right)^{1/2} S\left(\frac{8\pi E_c}{\hbar\omega_0}\right)^2 \left(\frac{8kT}{\pi m}\right)^{1/2} \left(\frac{\pi^2 E_c}{kT}\right)^{1/6} e^{-3(\pi^2 E_c/kT)^{1/3} + (\hbar\omega_0/2kT)} \quad (95)$$

where the cross section S is

$$S = \frac{\frac{\pi L^2}{9} \left(\ln \frac{\bar{A}^3}{\pi^2 k^2 T^2 E_c}\right)^2}{1 - \frac{6}{\ln(\bar{A}^3/\pi^2 k^2 T^2 E_c)}} \quad (96)$$

and the characteristic energy E_c is

$$E_c = \frac{m\omega^2 L^2}{2} \quad (97)$$

The constant β_{10}^2 is given by

$$\beta_{10}^2 = \frac{m}{16\mu} \frac{\hbar\omega_0}{E_c} \frac{\delta^4}{\sinh^2 \delta} \left[\left(\frac{2}{15} + \frac{\delta^2}{35} + \frac{\delta^4}{630}\right) + \left(\frac{1}{30} + \frac{\delta^2}{105} + \frac{2\delta^4}{2835}\right) \overline{R(-1,2)} + \left(\frac{\delta^4}{22,680}\right) \overline{R(-1,4)}\right] \quad (98)$$

where

25

$$\overline{R(-1, |\Delta l|)} = 1 - \sqrt{\pi} \ g \ e^{g^2}(1 - erf[g]) + (1 - \lambda g)^{7/3}\left[1 + \sqrt{\pi} \ g \ e^{g^2}(1 + erf[g])\right]$$

$$(99)$$

with $\lambda = (2B|\Delta l|/\hbar\omega_0)(kT/B)^{1/2}$ and $g = \lambda(\pi^2 E_c/kT)^{1/3}$.

These results will later be used to make some comparisons with experiment, and to deduce some values of the potential parameters $\overline{A}$ and L which best fit vibrational relaxation data.

CONSERVATION OF TOTAL ENERGY

We now consider the effects produced when conservation of energy is extended to include both the inelastic transfer of energy that occurs when vibrational transition occurs, and the elastic but nonadiabatic transfer of energy that occurs because the vibrational mode is transiently excited by collision (refs. 21, 22). In the following discussion an *elastic* collision is defined as one where no net change of kinetic energy is produced. The elastic collision may be *adiabatic*, meaning that internal modes of energy do not participate in the collision process; or the elastic collision may be *nonadiabatic*, in which case the internal modes of energy participate transiently. The *inelastic* collision is one where permanent transition occurs in one or more modes of internal energy, with a corresponding net change in kinetic energy. All inelastic collisions are also nonadiabatic, of course.

The usual perturbation used in semiclassical and classical analysis of the vibrational excitation problem is elastic and adiabatic in form, but, as pointed out earlier, the inelastic quality of the collision is approximately accounted for by letting the effective collision velocity be the average of initial and final velocities. This simple stratagem does not fully account for inelastic and nonadiabatic effects, however. The perturbation is also asymmetrically distorted by the transition, and, in addition, the vibrational modes of the diatomic molecule are transiently excited during collision, whether or not transition occurs (refs. 21, 22). The corrections required because of these inelastic and nonadiabatic collision effects will next be assessed.

Effects of Asymmetrical Distortions to the Collision Trajectory

When the collision is not adiabatic, the trajectory is asymmetrically distorted by permanent transfer of energy from or to the kinetic mode, and the classical conservation equation for energy

$$E = T + U \qquad (100)$$

does not hold. In this case, U is a skewed function and such an asymmetric function may be represented by

$$U = \overline{U}_o e^{-\left(\frac{r-\sigma}{L}\right)} = \varepsilon E e^{qt} \, \text{sech}^2 \, at \tag{101}$$

where q is a constant. With this form for the potential, the relative velocity between collision partners is

$$\frac{\dot{r}}{L} = 2a \tanh at - q \tag{102}$$

and the constants a and q may be made to fit the limiting conditions $\dot{r}(-\infty) = -u_i$ and $\dot{r}(\infty) = u_f$.

$$a = \frac{u_i + u_f}{4L}$$

$$q = \frac{u_i - u_f}{2L}$$

For the transitions of interest, one quantum of energy is involved so that

$$\frac{m}{2}(u_i^2 - u_f^2) = \pm\hbar\omega$$

and this equation can be combined with the two previous equations to yield

$$\frac{q}{a} = \frac{2(u_i^2 - u_f^2)}{(u_i + u_f)^2} = \pm\frac{\hbar\omega}{2E} \tag{103}$$

The probability of a transition is appreciable only when the collision energy, E, is large compared with $\hbar\omega$, and so, only when $q/a \ll 1$.

With the interaction potential of equation (101), the transition probability is

$$P^*_{v,v\pm1} = \beta^2_{v,v\pm1} \left(\frac{\varepsilon E}{\hbar\omega}\right)^2 |F^*|^2 \tag{104}$$

where

$$F^* = \omega \int_{-\infty}^{\infty} e^{qt} \, \text{sech}^2 \, at \, e^{i\omega t} \, dt \tag{105}$$

This transform is evaluated in appendix B, where it is found that

$$|F^*|^2 = 4\pi^2\left(\frac{\omega}{a}\right)^4 \left(1 + \frac{q^2}{\omega^2}\right) e^{-\pi\omega/a} \tag{106}$$

Therefore,

$$P^* = \left(\beta \frac{\varepsilon}{\hbar} \frac{mu^2}{2} \frac{2\pi\omega}{a^2}\right)\left(1 + \frac{q^2}{\omega^2}\right) e^{-\pi\omega/a} \qquad (107)$$

Except for the factor $[1 + (q^2/\omega^2)]$, this expression for the transition probability is the same as the earlier (eq. (47)) result which follows from an assumed adiabatic trajectory. This factor $(q/\omega)^2$ represents the correction for skewness in the shape of the interaction potential, and its size is easily estimated with the aid of equations (97) and (103).

$$\left(\frac{q}{\omega}\right)^2 = \left(\frac{q}{a}\right)^2\left(\frac{a}{\omega}\right)^2 = \frac{(\hbar\omega)^2}{16EE_c} \qquad (108)$$

For collisions of interest, $(\hbar\omega/E_c) < 10^{-1}$ and $(\hbar\omega/E) \ll 1$, and so

$$\left(\frac{q}{\omega}\right)^2 \approx 10^{-3}$$

This size for the correction factor leads to the conclusion that the major effect of distortions to the trajectory induced by vibrational transitions is accounted for by defining (refs. 19, 20) the effective collision velocity, u, to be

$$u = \frac{u_i + u_f}{2}$$

and that the transition probability is only slightly affected by the asymmetrical part of the distortion.

Effects of Adiabatic Symmetrical Distortions

In order to examine the effect of trajectory distortion caused by temporarily stored vibrational energy, it is first necessary to develop an expression for this quantity, V, as a function of time. This is done in appendix C with the help of simple relations, found by Kerner (ref. 24), for the energy excited in a classical oscillator and quantum transition probabilities for a harmonic oscillator. For transitions from the ground state (on which interest is here centered for comparison with observed relaxation data), the total number of vibrational quanta excited in all states is given by exactly the same expression as by small perturbation quantum theory,

$$V(t) = \hbar\omega P(t) = \beta^2 \frac{\omega}{\hbar} \left| \int_{-\infty}^{t} U(t)e^{i\omega t} \, dt \right|^2 \qquad (109)$$

In this equation, the subscripts 0, 1 on P and β are omitted for convenience, and it is assumed that U is an exponential interaction potential. Also in appendix C, the coefficients of the expansion of $V(t)$ about the turning point ($t = 0$) are found by differentiating equation (109).

$$V(t) = V_0 + \dot{V}_0 t + \frac{1}{2} \ddot{V}_0 t^2 + \ldots$$

$$V_0 = \frac{\beta^2 U_0{}^2}{\hbar\omega} \tag{110a}$$

$$\dot{V}_0 = \ddot{V}_0 = \dddot{V}_0 = 0 \tag{110b}$$

$$V_0^{iv} = \frac{2\beta^2\omega}{\hbar} U_0 \ddot{U}_0 \tag{110c}$$

Next, an interaction potential $U^*(t)$ will be found which simultaneously produces the correct vibrational excitation and satisfies the conservation of total energy

$$E = T + U^* + V$$

Again the assumption is made that the potential is of simple exponential form

$$U^*(t) = U_0^* \exp\left\{ - \left[\frac{r(t) - \sigma}{L} \right] \right\} \tag{111}$$

but $r(t)$ in this equation is distorted from its usual adiabatic collision value. Then

$$\dot{U}^* = - \frac{\dot{r}}{L} U^* \tag{112}$$

which may be combined with

$$T = \frac{m\dot{r}^2}{2}$$

to give

$$T = \frac{mL^2}{2} \left(\frac{\dot{U}^*}{U^*} \right)^2 \tag{113}$$

This expression for the kinetic energy in the conservation equation yields

$$V(t) = E - \left[\frac{mL^2}{2} \left(\frac{\dot{U}^*}{U^*} \right)^2 + U^* \right] \tag{114}$$

This equation is evaluated at the turning point and combined with equation (110a) to give

$$V_0 = E - \left[\frac{mL^2}{2} \left(\frac{\dot{U}_0^*}{U_0^*} \right)^2 + U_0^* \right] = \frac{\beta^2 U_0^{*2}}{\hbar\omega} \tag{115}$$

But equation (112) shows $\dot{U}_0^* = 0$ since $\dot{r}_0 = 0$, and so equation (115) may be solved for U_0^*.

$$U_0^* = \frac{\hbar\omega}{2\beta^2} \left(-1 + \sqrt{1 + \frac{4\beta^2 E}{\hbar\omega}} \right) \tag{116}$$

This same procedure may be used to find values for higher derivatives of U^* at the turning point when equation (114) has been differentiated repeatedly. For example, after it is differentiated twice,

$$\ddot{V}_0 = mL^2 \left[\frac{5\dot{U}_0^* \ddot{U}_0^*}{U_0^{*3}} - \left(\frac{\ddot{U}_0^*}{U^*} \right)^2 - \frac{\dot{U}_0^* \dddot{U}_0^*}{U_0^{*2}} - 3 \left(\frac{\dot{U}_0^*}{U^*} \right)^4 \right] - \ddot{U}_0^* \tag{117}$$

This equation is solved for $\ddot{U}_0^*$ by using $\ddot{V}_0 = 0$ from equation (110b).

$$\ddot{U}_0^* = - \frac{U_0^{*2}}{mL^2} \tag{118}$$

Similarly,

$$\dddot{U}_0^* = 0 \tag{119}$$

$$U_0^{* iv} = \frac{4U_0^{*3}}{m^2 L^4} - \frac{2}{3} \frac{\beta^2 U_0^{*3} \omega}{\hbar m L^2} \tag{120}$$

and higher derivatives can be found, if necessary.

Return, now, to the exponential dependence of $U^*(t)$ on $r(t)$ in equation (111). For an adiabatic collision trajectory,

$$\exp\left\{ - \left[\frac{r(t) - \sigma}{L} \right] \right\} = \text{sech}^2 at$$

with $a = u/2L$. This makes plausible the functional form for nonadiabatic collision, that is, one where the internal modes of the colliding partners take part in the energy transfer

30

$$\exp\left\{-\left[\frac{r(t) - \sigma}{L}\right]\right\} = \phi(t)\,\text{sech}^2\,at$$

when r(t) is distorted by transiently stored vibrational energy. Therefore, it is assumed that

$$U^*(t) = U_0^*\phi(t)\,\text{sech}^2\,at \tag{121}$$

The function $\phi(t)$ is near unity since the collision energy is large when compared with the stored vibrational energy, and it is not unduly restricted by the assumption, physically realistic, that $\phi(t) \rightarrow$ constant as $|t| \rightarrow \infty$. This last assumption is used with the derivative of equation (121) to give $a = u/2L$ as before.

The transition probability, P^*, is influenced most strongly by the behavior of $U^*(t)$ near the turning point, and the expansion

$$U^*(t) = U_0^*\,\text{sech}^2\,at\left\{\phi_0 + \dot{\phi}_0 t + \frac{1}{2}\ddot{\phi}_0 t^2 + \ldots\right\} \tag{122}$$

will be sought. The first coefficient is found to be

$$\phi_0 = 1 \tag{123}$$

by evaluating equation (121) at the turning point. The first derivative of equation (121), also evaluated at the turning point, reduces to

$$\dot{U}_0^* = U_0^*\dot{\phi}_0$$

and since $\dot{U}_0^* = 0$, it follows that

$$\dot{\phi}_0 = 0 \tag{124}$$

Further differentiation of equation (121) and use of equations (118), (119), and (120) gives the expressions

$$\ddot{\phi}_0 = \frac{\ddot{U}_0^*}{U_0^*} + 2a^2 = -\frac{U_0^*}{mL^2} + 2a^2 \tag{125a}$$

$$\dddot{\phi}_0 = 0 \tag{125b}$$

$$\phi_0^{iv} = \frac{4U_0^{*3}}{m^2L^4} - \frac{2}{3}\frac{\beta^2 U_0^{*3}\omega}{\hbar mL^2} + 12a^2\ddot{\phi}_0 - 16a^4 \tag{125c}$$

The expansion for $\phi(t)$ can be written

$$\phi(t) = 1 + c(at)^2 + d(at)^4 + \ldots$$

where

$$c = \frac{\ddot{\phi}_0}{2a^2}$$

and

$$d = \frac{\phi_0^{iv}}{24a^4}$$

and will be terminated after the term containing t^4. This is justified by the fact that only the behavior of $\phi(t)$ inside the interval $|at| \leq 2$ is important. Outside this interval, $\text{sech}^2 at$ changes very slowly, and since $\phi(t) \text{sech}^2 at$ must remain close to $\text{sech}^2 at$, its Fourier transform

$$F^* = \omega \int_{-\infty}^{\infty} \phi(t) \text{sech}^2(at) e^{i\omega t} \, dt \tag{126}$$

receives nearly its full magnitude from $-2 \leq at \leq 2$. Therefore, it is taken that

$$U^*(t) = U_0^* \text{sech}^2(at)[1 + c(at)^2 + d(at)^4] \tag{127}$$

is the interaction potential which produces the correct amount of stored vibrational energy and, at the same time, satisfies total energy conservation. The evaluation of its Fourier transform, F^*, to obtain the transition probability proceeds by contour integration.

In order that F^* may be evaluated, the integrals

$$f_n = \int_{-\infty}^{\infty} t^n \text{sech}^2(at) e^{i\omega t} \, dt = \frac{1}{a} \int_{-\infty}^{\infty} \left(\frac{x}{a}\right)^n \text{sech}^2 x \, e^{(i\omega/a)x} \, dx \tag{128}$$

must be found. But these integrals can be treated in the same manner, using the same contour and limiting process, as is used in appendix B for a slightly different integrand. The residue at the isolated singularity inside the contour is

$$R_n = \left(\frac{\pi i}{2a}\right)^{n-1} \left(\frac{\pi \omega}{2a} - n\right) \left(\frac{1}{a^2}\right) e^{-(\pi\omega/2a)} \tag{129}$$

and for $\omega/a \gg 1$,

$$f_n = 2\pi i R_n \approx \frac{\pi^{n+1} i^n \omega}{2^{n-1} a^{n+2}} e^{-\pi\omega/2a}$$

so that

$$F^* = 2\pi \left(\frac{\omega}{a}\right)^2 e^{-\pi\omega/2a} \left(1 - \frac{\pi^2 c}{4} - \frac{\pi^4 d}{16}\right) \qquad (130)$$

and

$$\left|F^*\right|^2 = 4\pi^2 \left(\frac{\omega}{a}\right)^4 e^{-\pi\omega/a} \left(1 - \frac{\pi^2 c}{4} - \frac{\pi^4 d}{16}\right)^2$$

If P^* is used to denote the corrected transition probability, after the temporarily stored vibrational energy is accounted for, then

$$P^* = \beta_{vv'}^2 \left(\frac{\varepsilon E}{\hbar\omega}\right)^2 \left|F^*\right|^2 \qquad (131)$$

and

$$\frac{P^*}{P} = \frac{\left|F^*\right|^2}{\left|F\right|^2}$$

However, when equation (130) is compared to equation (46) whose right hand side is F/ω, this ratio is seen to be

$$\frac{\left|F^*\right|^2}{\left|F\right|^2} = \left(1 - \frac{\pi^2 c}{4} - \frac{\pi^4 d}{16}\right)^2$$

and therefore

$$P^* = \left(1 - \frac{\pi^2 c}{4} - \frac{\pi^4 d}{16}\right)^2 P \qquad (132)$$

where P is the transition probability of equation (47), and where

$$c = \frac{\beta^2 E}{\hbar\omega}$$

$$d = \frac{2}{3}\left[-1 + \left(\frac{U_o^*}{E}\right)^2\right] - \frac{1}{36a^2}\left(\frac{U_o^*}{E}\right)\left(\frac{\beta^2 U_o^*}{\hbar\omega}\right)\left(\frac{\omega}{a}\right)^2 + c$$

The effect of the correction factor is to make, roughly,

$$P* \approx \frac{2}{5} P \qquad (133)$$

Consequently, the collision cross section, S* (eq. (4)), and the rate coefficient, $\alpha*$ (eq. (5)), are diminished by this same factor. But, the decreased rate coefficient implies (cf. eq. (6)) a relaxation time, $\tau*$, which is about 5/2 times τ, the relaxation time predicted by the theory which does not incorporate the effect of the temporarily stored vibrational energy.

COMPARISON WITH EXPERIMENT

There is no lack of data on rates of vibrational relaxation as a function of temperature (ref. 7). The experimentally determined quantity is the relaxation time τ, and according to equation (6) the product of τ and the pressure p is

$$p\tau = \frac{kT}{\alpha_{10}\left[1 - e^{-(\hbar\omega/kT)}\right]} \qquad (134)$$

In this equation α_{10} is the rate coefficient for transitions from the first excited state to the ground state, given by equation (95). This connection between the analytically derived α and the experimentally obtained τ provides a means for testing the analysis. At the same time, it yields a method for determining effective values for the molecular potential parameters, $\overline{A}$ and L.

The procedure begins with selecting a molecular species and collision partner and assuming trial values for $\overline{A}$ and L to describe the intermolecular potential. Thereupon, the rate coefficient $\alpha_{10}(T, \overline{A}, L)$ from equation (95) determines, through equation (100), a relaxation time τ which can be computed for chosen values of temperature and unit pressure. These computed values will be (nearly) collinear on a Landau-Teller plot, and the slope and ordinate of this line can be adjusted by changing the trial values for $\overline{A}$ and L. A combination of values for $\overline{A}$ and L can be determined by eye which produces the best agreement between the theoretical line and experimental data. This combination is taken to be an acceptable approximation to the effective values of these parameters. An example of the result of this procedure is shown in figure 6 for O_2-Ar collisions and in figure 7 for N_2-N_2 collisions.

It will be noticed in figure 7 that the slope of the $p\tau$ line is not quite correct for perfect agreement between theory and experiment. This observation leads to the suspicion that further adjustment of $\overline{A}$ and L will yield even better agreement than is shown, but this is not the case. Further adjustment to improve the slope moves the line vertically and degrades the overall agreement. Also shown in figure 7 is the relaxation time predicted for the delta function potential calculated by Meador (ref. 30). This predicted relaxation time is the order of 100 times larger than observed, and some remarks will be made later about this difference.
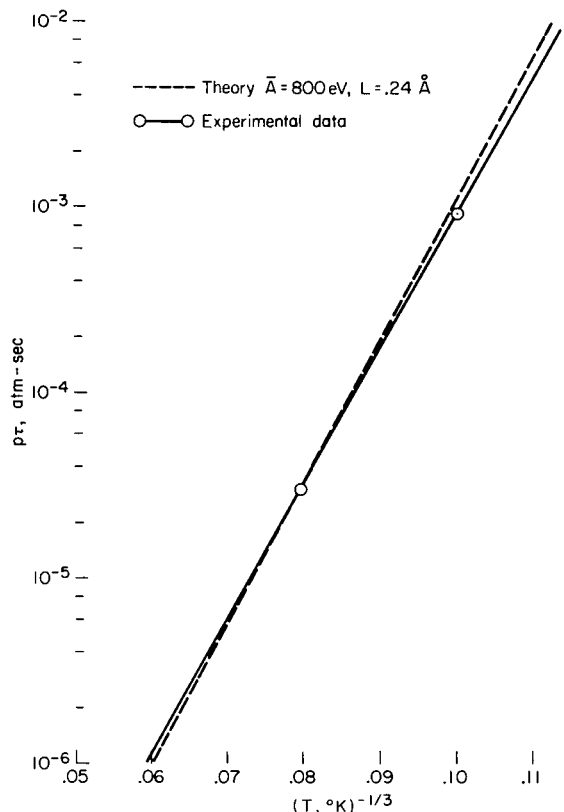
34

Figure 6.- Landau-Teller plot of vibrational relaxation for O_2-Ar collisions.
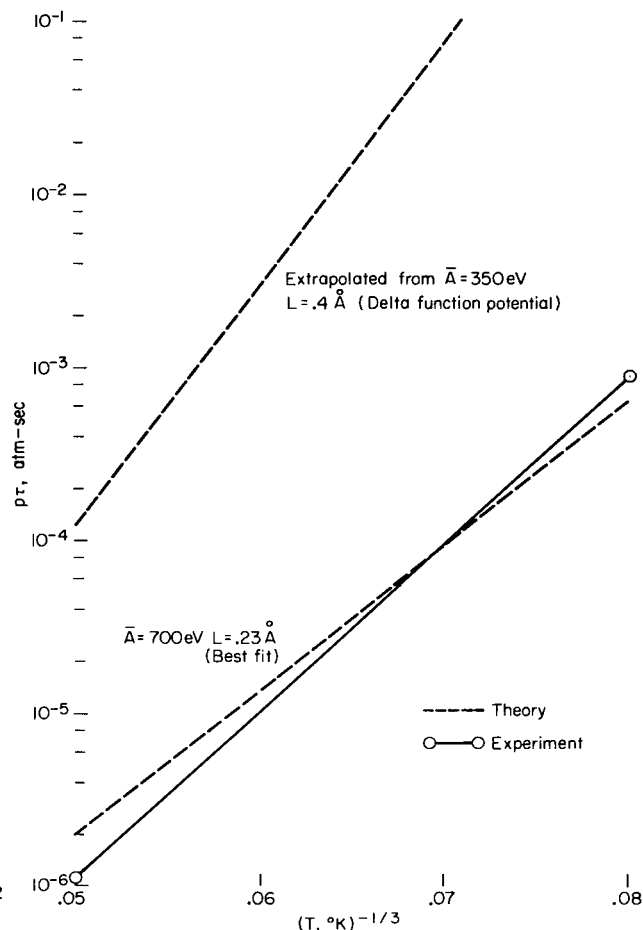

Figure 7.- Landau-Teller plot of relaxation time for N_2-N_2 collisions.

The above procedure has been applied to a variety of diatomic species undergoing collisions with an atomic or diatomic collision partner. The results are given in table 1 where two sets of intermolecular potential parameters are shown. The pair $\bar{A}, L$ were deduced using the semiclassical method without correction for conservation of total energy, and when this correction was made, their counterparts $\bar{A}^*, L^*$ were obtained. Comparison of these pairs shows that the sizable difference found earlier

$$\tau^* \approx \frac{5}{2} \tau$$

produces only slightly deviating forms for the exponential intermolecular potential. Close numerical agreement of the two sets of constants makes it difficult to ascertain which pair furnishes better agreement between experiment and theory. Hence, the pair $\bar{A}, L$ produced by the more simple, uncorrected semiclassical theory will be used in the remainder of this paper. Care must be taken in using these values for the constants at extrapolated temperatures. Neither the experimental data nor assumptions made in the

35

analysis can be meaningfully extended to temperatures sufficiently high for dissociation to become a competing process with vibrational excitation.

The accuracy of the values given for $\overline{A}$ and L cannot be assessed quantitatively. A possible approach to constructing table 1 is to find combinations of $\overline{A}$ and L that make the $p\tau$ line fit the experimental data best in the least squares sense. However, the numerical problem posed by this approach has proven to be without a distinct solution. There is a spectrum of combinations of $\overline{A}$ and L that appear to be equally valid from a numerical least squares standpoint. Other numerical attempts have also proved disappointing, and it was necessary that the $p\tau$ line be fit to the data subjectively. However, experience in choosing trial values for $\overline{A}$ and L gives assurance that the "best" value for L can be determined within 10-25 percent and for $\overline{A}$ within a factor of 2 or 3. In general, the more stringent confidence limits apply for heavier collision partners.

Attempts to evaluate $\overline{A}$ and L for the halogen gases were without reward for Br_2 - Br_2 and I_2 - I_2 collisions, and there is near-indeterminacy for Cl_2 - Cl_2. The experimental data (ref. 31) for these gases are obtained by a measurement of sound absorption at temperatures very low relative to the other data. A Landau-Teller plot of the halogen data is, anomalously, a nearly horizontal line. Except for chlorine, no combination of $\overline{A}$ and L predicts a slope small enough to give meaningful agreement, and even for Cl_2 the values of L required to fit the data seem to be abnormally small (the order of 0.05 Å).

A direct numerical comparison of experimental and calculated $p\tau$-values is made in table 2. The computed values were obtained using the combination of $\overline{A}$ and L found in table 1. It is to be noted that the comparison is made at temperatures which lie at or near the ends of the temperature range where $\overline{A}$ and L are fit to the experimental data. These are the temperatures where $p\tau_{exptl}$ and $p\tau_{calc}$ differ most (see figs. 6 and 7) in that range. Consequently, table 2 gives bounds for the discrepancy between theory and experiment. Also, since $p\tau$ varies linearly with $T^{-1/3}$ on a Landau-Teller plot, table 2 can be used to construct a counterpart to figures 6 and 7 for any of the species listed.

Strictly speaking, the CO data should be evaluated with a more general theory for heteronuclear molecules, since the effective potentials for C and O atom interactions can be different. Corrections for the asymmetrical center of mass should be small in this case, however, and the homonuclear molecule theory may be expected to give an approximate average interaction potential, corresponding to the random orientation of the molecular axis that occurs in the experiment. Dipole interactions affect the long range forces, but probably do not contribute largely to the steep part of the potential responsible for vibrational transitions.

Fitting vibrational relaxation data is widely conceded to be a rather inaccurate way to determine intermolecular potentials. Nevertheless, such potentials are so urgently needed for analysis of a wide variety of atomic and

TABLE 1.- VALUES OF THE POTENTIAL PARAMETERS $(\overline{A}, L)$ AND $(\overline{A}^*, L^*)$

Species	Partner	$\overline{A}$(eV)	L(Å)	$\overline{A}^*$(eV)	L^*(Å)	Approximate range of T, °K
O_2	O_2	800	0.19	900	0.18	500-5,000
O_2	Ar	800	.24	900	.23	1,000-5,000
O_2	He	550	.26	600	.26	300-2,000
O_2	H_2	300	.27	300	.26	300-2,000
N_2	N_2	700	.23	800	.21	2,000-8,000
CO	CO	850	.19	900	.18	1,200-6,000
CO	H_2	300	.28	350	.27	300-2,000
CO	He	400	.27	500	.26	300-2,000
Calculated delta function model						
O_2	O_2	147	0.47			1,000-10,000
N_2	N_2	350	.40			1,000-10,000

TABLE 2.- COMPARISON OF EXPERIMENTAL AND CALCULATED RELAXATION TIMES

Species	Collision partner	T, °K	$T^{-1/3}$	pτ, atm-sec	
				Experimental	Calculated
O_2	O_2	5000	0.058	4.0×10^{-7}	5.8×10^{-7}
		2000	.079	6.0×10^{-6}	7.2×10^{-6}
		1000	.1	1.0×10^{-4}	1.2×10^{-4}
		500	.126	2.5×10^{-3}	2.2×10^{-3}
O_2	Ar	2000	.079	3.0×10^{-5}	3.1×10^{-5}
		1000	.1	8.9×10^{-4}	1.2×10^{-3}
O_2	He	1500	.087	1.0×10^{-6}	0.5×10^{-6}
		300	.149	4.0×10^{-5}	6.0×10^{-5}
O_2	H_2	1000	.1	3.8×10^{-7}	3.2×10^{-7}
		300	.149	2.4×10^{-6}	3.7×10^{-6}
N_2	N_2	5000	.058	6.6×10^{-6}	9.3×10^{-6}
		2000	.079	7.4×10^{-4}	5.3×10^{-4}
CO	CO	5000	.058	1.9×10^{-6}	2.5×10^{-6}
		2000	.079	6.8×10^{-5}	6.6×10^{-5}
CO	He	1000	.1	2.9×10^{-5}	2.7×10^{-5}
		300	.149	2.6×10^{-3}	3.0×10^{-3}
CO	H_2	1000	.1	2.8×10^{-6}	2.9×10^{-6}
		300	.149	6.8×10^{-5}	6.8×10^{-5}

molecular problems, and so little information about these potentials exists, that there is always a strong temptation to evaluate the potentials as done in table 1, just to see what relations appear.

First of all, the results are generally consistent with similar attempts made with one-dimensional vibrational excitation theories. Any one-dimensional theory can only be used to determine L, not $\bar{A}$, since it can fit only the slope and not the absolute magnitude of the data on a Landau-Teller plot. Schwartz, Slawsky, and Herzfeld (ref. 11) obtained reasonable agreement with data (within a factor of 20 or so) when they chose L to fit the repulsive part of a Lennard-Jones potential, $U = \varepsilon[(r_0/r)^{12} - (r_0/r)^6]$. They found that $L \simeq r_0/17.5$, and for values of r_0 determined from relatively low-temperature viscosity data (ref. 32) this gives $L \simeq 0.2$ Å for O_2, N_2, and CO. Benson and Berend (ref. 33) chose to fit the repulsive part of a Morse potential, $U = U_0[(1 - e^{-ar})^2 - 1]$, and they presented values of a that best fit measured vibrational transition rates. In this case, $L \simeq 1/2a$, or $L \simeq 0.25$ Å for O_2, N_2, and CO. Rapp and Sharp (refs. 21,22) and Treanor (refs. 25,26) both used $L = 0.2$ Å for their calculations of N_2-N_2 vibrational excitation. These values are about the same as given in table 1 and are within the uncertainty inherent in fitting the data.

However, it seems to have generally been overlooked that all of these results from vibrational relaxation theory are different from estimates of N_2-N_2 and O_2-O_2 potentials that have been deduced by other methods. Mason and Vanderslice (refs. 34, 35) developed a delta function model for calculating short range intermolecular forces, and Meador (ref. 30) refined this method and applied it to N_2-N_2 collisions, showing that it agrees well with the potential for such collisions given by Amdur, Mason, and Jordan (ref. 36), who deduced this potential somewhat indirectly from Ar-N_2 and He-N_2 scattering measurements. Meador (ref. 30) then applied this same delta function model to O_2-O_2 collisions; in this case experimental verification is lacking. Meador's values of $\bar{A}$ and L are listed in table 1, and it can be seen that L is considerably larger than deduced from vibrational relaxation while $\bar{A}$ is smaller. At the collision energies of interest (0.1 - 1.0 eV), the delta function potential is less steep and of longer range. The shallower potential results in a more adiabatic collision, smaller excitation probability, and larger relaxation time (as shown in fig. 7). The expansions involved become doubtful for these large values of L, so the exact numerical results for Meador's potential should not be taken too seriously, but the qualitative effects should be valid, at least.

The disagreement between the potentials is not surprising, when one considers that a multiplicity of interaction potentials exist for molecular collisions, just as for atomic collisions, depending upon how the orbital and spin momentum vectors add up. Scattering is primarily produced by the long-range outer potentials that correspond to the largest total spin and degeneracy, such as calculated by Meador (ref. 30). On the other hand, vibrational transitions are undoubtedly due to interactions that proceed along shorter range, steeper potentials that occur when some of the spins are paired, and vibrational relaxation rates are presumably telling us something about the shape of these inner potentials. However, a number of factors prevent us from

deducing precise quantitative values for these inner potentials from vibrational relaxation data. Perhaps the most serious is that the semiclassical method uses the spherical average of the true potential and does not account for energy adiabatically transferred to and from the vibrational mode during the course of the collision. This effect is dramatically shown in the numerical calculations of Sharp and Rapp (ref. 22). The perturbation is not really the simple adiabatic scattering impulse assumed in equation (35), even though this shape has been traditionally used in all semiclassical analysis of the problem, but is distorted by the temporary transfer of energy into high-order vibrational modes, and is also slightly skewed by that small portion of the energy transferred irreversibly. Even where changes in impulse shape are relatively small, the effects on the Fourier transform can be sizable. Thus, the potential deduced from vibrational relaxation measurements should be thought of as an "effective" potential which incorporates the effect of energy stored in the vibrational mode, and it should not be interpreted as a pure interaction potential.

Several other approximations involved in the theory may be sources of error also, particularly at higher temperatures. One of these is due to the fact that small perturbation probabilities become the order of 0.1 at the velocities u_m for the highest temperature data, and at this point become sizably greater than the actual transition probabilities (refs. 24, 26). However, this error is compensated because multiple step transitions occur at these temperatures, and the total energy transferred is the same in either case. A second error which decreases the relaxation rate at high temperature occurs because the upper limit of the integral for the cross section is then finite, leading to the result of equation (60), rather than the approximation of equation (61) which is valid for very small transition probabilities. A third error occurs at high collision energies because the expression for the perturbation potential (eq. (19)) should include higher order terms in the expansion of the distances r_1 and r_2. Finally, the real interaction potentials are not simple exponentials. Thus, different effective values of L and $\bar{A}$ could be used for different ranges of temperature and adjusted to fit data exactly.

In spite of the uncertain interpretation of the potentials used, the simple theory can be fit to observed vibrational relaxation data reasonably well. The best fit is excellent when the colliding partner is an inert atom such as Ar or He, which is the type of collision that the theory is designed to describe. The correlations are only a little worse for collisions such as O_2-O_2 and N_2-N_2. The principal point to be emphasized is that the "effective potentials" deduced from these correlations are not necessarily realistic for other purposes.

DISCUSSION OF RESULTS

Perhaps the most satisfying result from this study of vibrational excitation is that the problem has been treated analytically in three dimensions, and the cross sections and the rate coefficients are expressed as

relatively simple functions of temperature and the interaction potential parameters only. To first order, the results show the same functional behavior as one-dimensional models. This behavior confirms the qualitative results in reference 16 and further justifies the widespread use of the one-dimensional model for analyzing vibrational relaxation data.

The relative simplicity of the semiclassical model compared with the method of partial waves (which gives slowly converging results in three-dimensional quantum treatments) has made it possible to retain fully analytic expressions all the way to the final rate coefficients. The results clearly show how vibrational transitions (predominantly $\Delta v = \pm 1$) are accompanied by simultaneous rotational transitions (predominantly $\Delta l = 0, \pm 2$), an aspect of the process that has often been ignored. The effect of these coupled rotational transitions increases the total vibrational transition rate from 50 to 100 percent at typical conditions. This effect went unnoticed in one-dimensional theory because it could simply be absorbed in the empirical steric factor involved in that theory. Herzfeld and Litovitz (ref. 37) and others have pointed out that such coupled rotations must occur in three-dimensional collisions, however. Also, the three-dimensional model permits one to evaluate effective values for both the scale factor $\overline{A}$ and the range factor L of the intermolecular potential by fitting vibrational relaxation data, whereas one-dimensional models permit only the factor L to be determined. Both models give about the same values for L, the order of 0.2 Å. The value of $\overline{A}$ given by the three-dimensional model is reasonable, the order of several hundred eV for typical interactions. These potentials are much steeper and of shorter range than known scattering potentials, and we suggest that this occurs primarily because vibrational transitions are produced most frequently when the interaction proceeds along one of the shorter range, steeper potentials that obtain when some of the electron spins involved are paired. However, the "effective" potential for vibrational relaxation should probably not be interpreted as a pure interaction potential in any case, since it also includes the effects of potential stored in high vibrational modes during collision.

Although the interpretation of the potentials derived may be questionable, the semiclassical theory of vibrational excitation can be fit reasonably well to most relaxation-rate data if the appropriate effective potential is chosen. The theory appears to contain enough realism to be suitable for investigating some other facets of the vibrational excitation problem; for example, the effects of anharmonicity, vibration-vibration exchange, heteronuclear molecules, and perhaps triatomic molecules.

The square of the transition matrix elements decreases in size fairly rapidly as $|\Delta l|$ increases, but the transition probability increases rapidly if Δv and Δl have opposed algebraic sign because the energy difference between states involved in the transition is then decreased. The combined effect of these two factors is that transition probabilities for $|\Delta l| = 0, 2$ are about equal, while those for $|\Delta l| = 4$ are about an order of magnitude smaller. Higher order perturbation terms can increase the later transitions somewhat and contribute some higher order, even number changes Δl as well,

but it appears that $\Delta l = 0, \pm 2$ will remain the dominant rotational transitions which are coupled to the vibrational transitions $\Delta v = \pm 1$.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., 94035, April 8, 1970

APPENDIX A

EVALUATION OF THE CONSTANTS $\beta^2(\Delta v, \Delta l)$

In this appendix, the overlap integral

$$\beta(v,l,m;v',l',m') = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{\rho=0}^{\infty} \psi^*(v',l',m') \left[\frac{\delta^2}{\sinh \delta}\left(\frac{\rho-\rho_e}{2L}\right)\left(\sin^2\theta\cos^2\phi\right.\right.$$

$$\left.\left. + \frac{\delta^2}{6}\sin^4\theta\cos^4\phi\right)\right]\psi_{(v,l,m)}\rho^2\sin\theta\,d\rho\,d\theta\,d\phi \tag{A1}$$

will be evaluated. The square, $\beta^2(v,l,m;v',l',m') \equiv \beta^2(v,l,m;v+\Delta v,l+\Delta l,m+\Delta m)$ will then be averaged over all possible values of m and, with the assumption that $l \gg 1$, it will be found that this average is independent of l. Thus, for vibrational transitions from a fixed vibrational level, the averaged squares are functions of Δv, Δl, and Δm only; $\beta^2(\Delta v, \Delta l, \Delta m)$. Since these squares are proportional to the transition probability, they may be combined in the manner probabilities are combined.

$$\beta^2(\Delta v, \Delta l) = \sum_{\Delta m} \beta^2(\Delta v, \Delta l, \Delta m)$$

EVALUATION OF THE OVERLAP INTEGRAL

The unperturbed wave functions $\psi_{(v,l,m)}(\rho,\theta,\phi)$ and $\psi_{(v',l',m')}(\rho,\theta,\phi)$ that appear in equation (A1) are, respectively, the wave functions of the rotating and vibrating diatomic molecule before and after the collision. For a rigid-rotator, harmonic oscillator these wave functions can be written:

$$\psi_{(v,l,m)}(\rho,\theta,\phi) = Y_{lm}(\theta,\phi)\left\{C_v \frac{1}{\rho} e^{-(\alpha/2)(\rho-\rho_e)^2} H_v\left[\sqrt{\alpha}(\rho-\rho_e)\right]\right\}$$

In this equation, $H_v[\sqrt{\alpha}(\rho-\rho_e)]$ is the vth Hermite polynomial and the $Y_{lm}(\theta,\phi)$ are spherical harmonics expressed in terms of $P_l^{|m|}(\cos\theta)$, the associated Legendre functions of the first kind.

$$Y_{lm}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} C_l^{|m|} P_l^{|m|}(\cos\theta)$$

The normalizing constants are expressed

$$C_{\mathcal{l}}^{|m|} = \left[\frac{2\mathcal{l}+1}{2} \frac{(\mathcal{l} - |m|)!}{(\mathcal{l} + |m|)!} \right]^{1/2} \tag{A2}$$

$$C_v = \left(\sqrt{\frac{\alpha}{\pi}} \frac{1}{v! 2^v} \right)^{1/2} \tag{A3}$$

where

$$\alpha = \frac{\mu\omega}{\hbar}$$

It is seen that equation (A1) can be written

$$\beta(v,\mathcal{l},m;v',\mathcal{l}',m') = \frac{\delta^2}{\sinh \delta} I_1 \int_{\theta=o}^{\pi} \int_{\phi=o}^{2\pi} Y_{\mathcal{l}'m'}^{*}(\theta,\phi) \left(\sin^3 \theta \cos^2 \phi \right.$$

$$\left. + \frac{\delta^2}{6} \sin^5 \theta \cos^4 \phi \right) Y_{\mathcal{l}m}(\theta,\phi) d\theta \, d\phi \tag{A4}$$

with

$$I_1 = \frac{1}{2L\alpha} \int_o^{\infty} C_v C_{v'} H_{v'}(x) H_v(x) x e^{-x} dx \qquad (x = \sqrt{\alpha}(\rho - \rho_e))$$

The orthonormal properties and recurrence relation for the Hermite polynomials which will be used to evaluate I_1 can be found in mathematical texts (e.g., ref. 38, p. 308). These properties are

$$\left. \begin{array}{ll} \int_o^{\infty} H_{v'}(x) H_v(x) e^{x^2} dx = 0 & (v \neq v') \\ \qquad\qquad = 2^v v! \sqrt{\pi} = \sqrt{\alpha}/C_v^2 & (v = v') \end{array} \right\} \tag{A5}$$

and

$$x H_v(x) = \frac{1}{2} H_{v+1}(x) + v H_{v-1}(x) \tag{A6}$$

When this last equation is multiplied by $e^{-x^2} H_{v'}(x)$ and then integrated over $(0, \infty)$, there is obtained

$$\int_o^{\infty} H_{v'}(x) H_v(x) e^{-x^2} x \, dx = \frac{1}{2} \int_o^{\infty} H_{v+1}(x) H_{v'}(x) e^{-x^2} dx + v \int_o^{\infty} H_{v-1}(x) H_{v'}(x) e^{x^2} dx \tag{A7}$$

43

When equation (A5) is used with equation (A7), it is seen that the right-hand side of (A7) is zero unless $v' = v \pm 1$. Therefore,

$$I_1 = \frac{C_{v'}C_v}{2L\alpha} \int_0^\infty H_{v'}(x)H_v(x)xe^{-x^2}\,dx = \frac{1}{2L}\sqrt{\frac{v+1}{2\alpha}} \qquad \text{when} \quad v'=v+1 \qquad \text{(A8a)}$$

$$= \frac{1}{2L}\sqrt{\frac{v}{2\alpha}} \qquad \text{when} \quad v'=v-1 \qquad \text{(A8b)}$$

$$= 0 \qquad \text{when} \quad v' \neq v \pm 1 \qquad \text{(A8c)}$$

The integral of equation (A1) may now be written

$$\beta(v,l,m;v',l',m') = \frac{\delta^2}{\sinh \delta}\frac{\sqrt{v+1,0}}{2L\sqrt{\alpha}}(I_2 + I_3) \qquad \text{(A9)}$$

where $(v + 1,0)$ is equal to $v + 1$ or v accordingly as $v' = v + 1$ or $v - 1$, and where

$$I_2 = \left[\frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\cos^2\phi\,d\phi\right]\left[C_{l'}^{|m'|}C_l^{|m|}\int_0^\pi P_{l'}^{|m'|}(\cos\theta)\sin^3\theta\,P_l^{|m|}(\cos\theta)d\theta\right]$$
$$\text{(A10)}$$

and

$$I_3 = \frac{\delta^2}{6}\left[\frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\cos^4\phi\,d\phi\right]\left[C_{l'}^{|m'|}C_l^{|m|}\int_0^\pi P_{l'}^{|m'|}(\cos\theta)\sin^5\theta\,P_l^{|m|}(\cos\theta)d\theta\right]$$
$$\text{(A11)}$$

The method for evaluating each of these integrals will be demonstrated separately. In order to facilitate notation in what follows, $|m|$ will be written as m.

(i) $$I_2 = \left[\frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\cos^2\phi\,d\phi\right]\left[C_{l'}^{m'}C_l^m\int_0^\pi P_{l'}^{m'}(\cos\theta)\sin^3\theta\,P_l^m(\cos\theta)d\theta\right]$$

The first integral in equation (A10) can be written

$$\frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\cos^2\phi\,d\phi = \frac{1}{2\pi}\left[\int_{-\pi}^\pi \cos(m-m')\phi\cos^2\phi\,d\phi + i\int_{-\pi}^\pi \sin(m-m')\phi\cos^2\phi\,d\phi\right]$$

44

The second integral on the right-hand side has symmetric limits and an integrand which is an odd function. Its value is therefore zero. To evaluate the first integral write $\cos^2 \phi = (1 + \cos 2\phi)/2$. Then

$$\frac{1}{2\pi} \int_0^{2\pi} e^{i(m-m')\phi} \cos^2\phi \, d\phi = \frac{1}{4\pi} \int_{-\pi}^{\pi} \cos(m-m')\phi \, d\phi + \frac{1}{4\pi} \int_{-\pi}^{\pi} \cos 2\phi \cos(m-m')\phi \, d\phi$$

The first integral on the right-hand side is equal to zero unless $m' = m$, in which case its value is 2π. The second integral is zero unless $m' = m \pm 2$, when its value is π. Hence, the chosen form of the interaction potential (eq. (19)) permits only the changes $m' = m$, $m + 2$, or $m - 2$ by a collision. Accordingly,

$$I_2 = \left\{ \begin{array}{ll} \frac{1}{2} & \text{if } \Delta m = 0 \\[2ex] \frac{1}{4} & \text{if } \Delta m = \pm 2 \end{array} \right\} \left[C_l^{m'} C_l^m \int_0^{\pi} P_l^{m'}(\cos \theta) P_l^m(\cos \theta) \sin^3 \theta \, d\theta \right]$$

If $x = \cos \theta$, then

$$C_l^{m'} C_l^m \int_0^{\pi} P_l^{m'}(\cos \theta) P_l^m(\cos \theta) \sin^3 \theta \, d\theta = I_{2,\theta} = C_l^{m'} C_l^m \int_{-1}^{1} P_l^{m'}(x)(1 - x^2) P_l^m(x) \, dx$$

The associated Legendre functions are orthogonal in $(-1, 1)$:

$$\int_{-1}^{1} P_{l'}^m(x) P_l^m(x) \, dx = 0 \qquad (l' \neq l) \tag{A12a}$$

$$= (C_l^m)^{-2} \qquad (l' = l) \tag{A12b}$$

They also satisfy the recurrence relations

$$\sqrt{x^2 - 1} \, P_l^{m+1}(x) = (l - m) x P_l^m(x) - (l + m) P_{l-1}^m(x) \tag{A13}$$

$$x P_l^m(x) = \frac{1}{2l+1} \left[(l - m + 1) P_{l+1}^m(x) + (l + m) P_{l-1}^m(x) \right] \tag{A14}$$

$$P_{l+1}^m(x) = P_{l-1}^m(x) + (2l + 1) \sqrt{x^2 - 1} \, P_l^{m-1}(x) \tag{A15}$$

These relations hold for real and complex x. For x in $[-1, 1]$, the radical $\sqrt{x^2 - 1}$ which appears in (A13) and (A15) is complex. However, these relations will be used to develop formulas involving $(1 - x^2)$ which is real in the interval.

It has been found that Δm can take on three possible values in I_2, $(\Delta m = 0, \pm 2)$, and for each of them, $I_{2,\theta}$ will have a separate value:

(a) $\quad I_{2,\theta}(l,l';0) = C_{l'}^m C_l^m \int_{-1}^{1} P_{l'}^m(x)(1 - x^2)P_l^m(x)\,dx$

(b) $\quad I_{2,\theta}(l,l';+2) = C_{l'}^{m+2} C_l^m \int_{-1}^{1} P_{l'}^{m+2}(x)(1 - x^2)P_l^m(x)\,dx$

(c) $\quad I_{2,\theta}(l,l';-2) = C_{l'}^{m-2} C_l^m \int_{-1}^{1} P_{l'}^{m-2}(x)(1 - x^2)P_l^m(x)\,dx$

Each case must be considered separately, and notation will further be abbreviated by writing $P_l^m(x) = P_l^m$.

$$\text{Case (a):} \quad I_{2,\theta} = C_{l'}^m C_l^m \left(\int_{-1}^{1} P_{l'}^m P_l^m \, dx - \int_{-1}^{1} P_{l'}^m x^2 P_l^m \, dx \right)$$

When the orthogonality property (A12) is applied to the first integral on the right-hand side of the above equation, it is seen that this integral is zero unless $l' = l$ when its value is $1/(C_l^m)^2$.

The second integral on the right can be evaluated by multiplying the recurrence relation (A14) by $(x P_{l'}^m)$, and then applying this same equation to the terms $x P_{l+1}^m$ and $x P_{l-1}^m$ which appear in the result. Finally, it is obtained that

$$P_{l'}^m x^2 P_l^m = \frac{l + m}{2l+1} \left\{ \frac{1}{2l-1} \left[(l - m)P_l^m P_{l'}^m + (l + m - 1)P_{l'}^m P_{l-2}^m \right] \right\}$$

$$+ \frac{l-m+1}{2l+1} \left\{ \frac{1}{2l+3} \left[(l - m + 2)P_{l'}^m P_{l+2}^m + (l + m + 1)P_{l'}^m P_l^m \right] \right\} \tag{A16}$$

When both sides of this equation are integrated over $(-1, 1)$, the orthogonality relation (A12) shows the right side of the resulting equation to be zero, except when $l' = l$ or $l + 2$ or $l - 2$; that is, for $\Delta l = 0$ or ± 2. The results are:

$$I_{2,\theta}(\Delta l = 0, \Delta m = 0) = 1 - \frac{(l+m)(l-m)}{(2l+1)(2l-1)} - \frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)} \tag{A17a}$$

46

$$I_{2,\theta}(+2,\theta) = -\left[\frac{(l-m+1)(l-m+2)(l+m+2)(l+m+1)}{(2l+1)(2l+3)^2(2l+5)}\right]^{1/2} \tag{A17b}$$

$$I_{2,\theta}(-2,\theta) = -\left[\frac{(l+m)(l+m-1)(l-m)(l-m-1)}{(2l+1)(2l-1)^2(2l-3)}\right]^{1/2} \tag{A17c}$$

Case (b): $I_{2,\theta}(l',l;+2) = C_{l'}^{m+2}C_l^m \int_{-1}^{1} P_{l'}^{m+2}(1-x^2)P_l^m \, dx$

In this case, the recurrence relations (A13) and (A14) are used to write $P_{l'}^{m+2}$ in terms of $P_{l'+2}^m$ and $P_{l'-2}^m$. The preliminary result of combining these two equations is

$$-\sqrt{x^2-1}\, P_l^{m+1} = \frac{1}{2l+1}\left[(l+m+1)(l+m)P_{l-1}^m - (l-m)(l-m+1)P_{l+1}^m\right] \tag{A18}$$

and from this equation comes

$$-\sqrt{x^2-1}\, P_l^{m+2} = \frac{1}{2l+1}\left[(l+m+2)(l+m+1)P_{l-1}^{m+1} - (l-m-1)(l-m)P_{l+1}^{m+1}\right]$$

This last equation is then multiplied by $\sqrt{x^2-1}$ and equation (A18) is applied to terms involving $\sqrt{x^2-1}\, P_{l-1}^{m+1}$ and $\sqrt{x^2-1}\, P_{l+1}^{m+1}$. Finally, it is derived that

$$(1-x^2)P_{l'}^{m+2} = \frac{(l'+m+2)(l'+m+1)}{2l'+1}\left[\frac{(l'+m-1)(l'+m)}{2l'-1}P_{l'-2}^m - \frac{(l'-m-1)(l'-m)}{2l'-1}P_{l'}^m\right]$$

$$-\frac{(l'-m-1)(l'-m)}{2l'+1}\left[\frac{(l'+m+1)(l'+m+2)}{2l'+3}P_{l'}^m - \frac{(l'-m+1)(l'-m+2)}{2l'+3}P_{l'+2}^m\right] \tag{A19}$$

This equation is multiplied by P_l^m and the resulting equation is integrated over $(-1, 1)$. It is seen once more that the orthogonality relation (A12) precludes rotational transitions in which l' is not equal to l or to $l \pm 2$. The results are:

$$I_{2,\theta}(0,+2) = -2\left[\frac{(l+m+2)(l+m+1)(l-m)(l-m-1)}{(2l+3)^2(2l-1)^2}\right]^{1/2} \tag{A20a}$$

$$I_{2,\theta}(+2,+2) = \left[\frac{(l+m+4)(l+m+3)(l+m+2)(l+m+1)}{(2l+5)(2l+3)^2(2l+1)}\right]^{1/2} \tag{A20b}$$

$$I_{2,\theta}(-2,+2) = \left[\frac{(l-m-3)(l-m-2)(l-m-1)(l-m)}{(2l+3)(2l-1)^2(2l+1)}\right]^{1/2} \tag{A20c}$$

Case (c): $\quad I_{2,\theta}(l',l;-2) = C_{l'}^{m-2}C_l^m \int_{-1}^{1} P_{l'}^{m-2}(1-x^2)P_l^m \, dx$

Here, the recurrence formula (A15) is used repeatedly to obtain

$$-P_l^m(1-x^2)P_{l'}^{m-2} = \frac{1}{(2l'+1)}\left(\frac{1}{2l'+3}P_l^m P_{l'+2}^m - \frac{1}{2l'+3}P_l^m P_{l'}^m - \frac{1}{2l'-1}P_l^m P_{l'}^m - \frac{1}{2l'-1}P_l^m P_{l'-2}^m\right)$$

and this equation is then integrated over $(-1,1)$ to get

$$I_{2,\theta}(0,-2) = +2\left[\frac{(l+m)(l+m-1)(l-m+2)(l-m+1)}{(2l+3)(2l-1)}\right]^{1/2} \tag{A21a}$$

$$I_{2,\theta}(+2,-2) = -\left[\frac{(l-m+4)(l-m+3)(l-m+2)(l-m+1)}{(2l+1)(2l+3)^2(2l+5)}\right]^{1/2} \tag{A21b}$$

$$I_{2,\theta}(-2,-2) = -\left[\frac{(l+m)(l+m-1)(l+m-2)(l+m-3)}{(2l+1)(2l-1)^2(2l-3)}\right]^{1/2} \tag{A21c}$$

This completes the evaluation of $I_2(l,l';m,m') = I_2(\Delta l,\Delta m)$, and it is seen that this integral can take on a total of nine different expressions, one for each combination of the three allowed changes, Δl, in the rotational quantum number and the three allowed changes, Δm, in the magnetic quantum number. If it is assumed that $l \gg 1$, each of these expressions can be simplified. For example, a reasonable approximation for $I_{2,\theta}(0,0)$, using $l \gg 1$, is

$$1 - \frac{(l+m)(l-m)}{(2l+1)(2l-1)} - \frac{(l-m+1)(l+m-2)}{(2l+1)(2l+3)} \approx 1 - \frac{2(l^2-m^2)}{4l^2} = \frac{l^2+m^2}{2l^2}$$

Therefore,

$$I_2(0,0) = \frac{1}{2}I_{2,\theta}(0,0) \approx \frac{l^2+m^2}{4l^2} \tag{A22a}$$

48

Similarly,

$$I_2(0,2) = \frac{1}{4} I_{2,\theta}(0,2) \approx - \frac{l^2-m^2}{8l^2} \tag{A22b}$$

$$I_2(0,-2) = \frac{1}{4} I_{2,\theta}(0,-2) \approx \frac{l^2-m^2}{8l^2} \tag{A22c}$$

$$I_2(2,0) = \frac{1}{2} I_{2,\theta}(2,0) \approx - \frac{l^2-m^2}{8l^2} \tag{A22d}$$

$$I_2(2,2) = \frac{1}{4} I_{2,\theta}(2,2) \approx \frac{(l+m)^2}{16l^2} \tag{A22e}$$

$$I_2(2,-2) = \frac{1}{4} I_{2,\theta}(2,-2) \approx - \frac{(l-m)^2}{16l^2} \tag{A22f}$$

$$I_2(-2,0) = \frac{1}{2} I_{2,\theta}(-2,0) \approx - \frac{l^2-m^2}{8l^2} \tag{A22g}$$

$$I_2(-2,2) = \frac{1}{4} I_{2,\theta}(-2,2) \approx \frac{(l-m)^2}{16l^2} \tag{A22h}$$

$$I_2(-2,-2) = \frac{1}{4} I_{2,\theta}(-2,-2) \approx - \frac{(l+m)^2}{16l^2} \tag{A22i}$$

(ii) $\quad I_3 = \frac{\delta^2}{6} \left[\frac{1}{2\pi} \int_0^{2\pi} \cos^4 \phi \; e^{i(m-m')\phi} \, d\phi \right] \left[C_{l'}^{m'} C_l^m \int_0^\pi P_{l'}^{m'}(\cos \theta)(\sin^5 \theta) P_l^m(\cos \theta) d\theta \right]$

The first integral on the right in the equation for I_3 can be written, with the use of $\cos^4 \phi = (1/8)\cos 4\phi + \cos^2 \phi - 1/8$, as

$$\frac{1}{2\pi} \int_0^{2\pi} \cos^4 \phi \; e^{i(m-m')\phi} \, d\phi = \frac{1}{2\pi} \int_{-\pi}^\pi \cos^2 \phi \cos(m-m')\phi \, d\phi - \frac{1}{16\pi} \int_{-\pi}^\pi \cos(m-m')\phi \, d\phi$$

$$+ \frac{1}{16\pi} \int_{-\pi}^\pi \cos 4\phi \cos(m-m')\phi \, d\phi$$

It was found earlier that

$$\frac{1}{2\pi} \int_{-\pi}^\pi \cos^2 \phi \cos(m-m')\phi \, d\phi = \left\{ \begin{array}{ll} \frac{1}{2} & \text{if } m' = m \\[2mm] \frac{1}{4} & \text{if } m' = m \pm 2 \\[2mm] 0 & \text{otherwise} \end{array} \right\}$$

49

Hence, after evaluating the second integral,

$$\frac{1}{2\pi} \int_0^{2\pi} \cos^4 \phi \; e^{i(m-m')\phi} \, d\phi = \begin{cases} \frac{3}{8} & \text{if } m' = m \\ \frac{1}{4} & \text{if } m' = m \pm 2 \\ 0 & \text{otherwise} \end{cases} + \frac{1}{16\pi} \int_{-\pi}^{\pi} \cos 4\phi \, \cos(m-m')\phi \, d\phi$$

The last integral vanishes unless $(m - m') = 4$, in which case its value is equal to π. Consequently,

$$\frac{1}{2\pi} \int_0^{2\pi} \cos^4 \phi \; e^{i(m-m')\phi} \, d\phi = \begin{cases} \frac{3}{8} & \text{if } m' = m \\ \frac{1}{4} & \text{if } m' = m \pm 2 \\ \frac{1}{16} & \text{if } m' = m \pm 4 \end{cases} \qquad (A23)$$

and the integral vanishes for all other values of m'.

When $x = \cos \theta$, the integral

$$I_{3,\theta} = C_l^{m'} C_l^m \int_0^\pi P_l^{m'}(\cos \theta)(\sin^5 \theta) P_l^m(\cos \theta) d\theta = C_l^{m'} C_l^m \int_{-1}^1 P_l^{m'}(x)(1 - x^2)^2 P_l^m(x) dx$$

Now

$$(1 - x^2)^2 = (1 - x^2) - x^2(1 - x^2)$$

so that $I_{3,\theta}$ becomes

$$I_{3,\theta} = C_l^{m'} C_l^m \int_{-1}^1 P_l^{m'}(1 - x^2) P_l^m \, dx - C_l^{m'} C_l^m \int_{-1}^1 P_l^{m'}[x^2(1 - x^2)] P_l^m \, dx$$

$$= I_{2,\theta} - C_l^{m'} C_l^m \int_{-1}^1 P_l^{m'}[x^2(1 - x^2)] P_l^m \, dx$$

Since $I_{2,\theta}$ has already been evaluated, it remains only to evaluate the integral

$$I'_{3,\theta} = C_l^{m'} C_l^m \int_{-1}^1 P_l^{m'}[x^2(1 - x^2)] P_l^m \, dx \qquad (A24)$$

In order to carry out this integration, the recursion relations obtained from equations (A15), (A16), and (A19) will be used. For example, if we use $l \gg 1$, equation (A16) may be written

$$P_l^m, x^2 P_l^m \approx \frac{1}{4l^2} \left[2(l^2 - m^2) P_l^m, P_l^m + (l + m)^2 P_l^m, P_{l-2}^m + (l - m)^2 P_l^m, P_{l+2}^m \right] \qquad \text{(A25)}$$

This equation is multiplied by x^2 to give

$$P_l^m, x^4 P_l^m \approx \frac{1}{4l^2} \left[2(l^2 - m^2) P_l^m, x^2 P_l^m + (l + m)^2 P_l^m, x^2 P_{l-2}^m + (l - m)^2 P_l^m x^2 P_{l+2}^m \right] \qquad \text{(A26)}$$

In similar ways there are obtained

$$P_{l'}^{m+2}, x^2(1 - x^2) P_l^m \approx \frac{1}{4l^2} \left[(l + m)^4 P_{l'-2}^m, x^2 P_l^m - 2(l^2 - m^2)^2 P_{l'}^m, x^2 P_l^m + (l - m)^4 P_{l'+2}^m, x^2 P_l^m \right]$$

$$\text{(A27)}$$

$$P_l^m x^2(1 - x^2) P_{l'}^{m-2} \approx \frac{1}{4l'^2} \left[2 P_l^m x^2 P_{l'}^m - P_l^m x^2 P_{l'+2}^m - P_l^m x^2 P_{l'-2}^m \right] \qquad \text{(A28)}$$

$$P_l^m(1 - x^2)^2 P_{l'}^{m-4} \approx \frac{1}{4l^2} \left[2 P_l^m(1 - x^2) P_{l'}^{m-2} - P_l^m(1 - x^2) P_{l'+2}^{m-2} - P_l^m(1 - x^2) P_{l'-2}^{m-2} \right] \qquad \text{(A29)}$$

It has been found that Δm can take on five possible values in I_3, ($\Delta m = 0, \pm 2, \pm 4$) and for each of these, $I'_{3,\theta}$ will have a separate value: $I'_{3,\theta}(\Delta l, 0)$, $I'_{3,\theta}(\Delta l, 2)$, $I'_{3,\theta}(\Delta l, -2)$, $I'_{3,\theta}(\Delta l, -4)$, $I'_{3,\theta}(\Delta l, 4)$.

Case (a): $\quad I'_{3,\theta}(\Delta l, 0) = C_l^m, C_l^m \int_{-1}^{1} P_l^m, x^2 P_l^m \, dx - C_l^m, C_l^m \int_{-1}^{1} P_l^m, x^4 P_l^m \, dx$

When equations (A25) and (A26) are integrated over (-1,1) and the usual orthogonality conditions are applied,

$$I'_{3,\theta}(0,0) \approx \frac{l^2 - m^2}{2l^2} - \frac{(l^2 - m^2)^2}{4l^4} - \frac{(l^2 - m^2)^2}{8l^4}$$

Therefore

$$I_{3,\theta}(0,0) = I_{2,\theta}(0,0) - I'_{3,\theta}(0,0) \approx 1 - \frac{l^2 - m^2}{2l^2} - \frac{l^2 - m^2}{2l^2} + \frac{3}{8} \frac{(l^2 - m^2)^2}{l^4}$$

and

$$I_3(0,0) \approx \frac{3}{8} \frac{\delta^2}{6} \left[1 - \frac{l^2-m^2}{l^2} + \frac{3}{8} \frac{(l^2-m^2)^2}{l^4} \right]$$

$$\approx \frac{1}{128 l^4} \left(3l^4 + 2l^2 m^2 + 3m^4 \right) \delta^2 \qquad (A30a)$$

In a similar way, it is found that

$$I_3(2,0) \approx - \frac{1}{64 l^2} (l^4 - m^4) \delta^2 \qquad (A30b)$$

$$I_3(-2,0) \approx - \frac{1}{64 l^4} (l^4 - m^4) \delta^2 \qquad (A30c)$$

$$I_3(4,0) \approx \frac{1}{256 l^4} (l^4 - 2l^2 m^2 + m^4) \delta^2 \qquad (A30d)$$

$$I_3(-4,0) \approx \frac{1}{256 l^4} (l^4 - 2l^2 m^2 + m^4) \delta^2 \qquad (A30e)$$

Further, it is seen from equations (A26) and (A25) that $I_{3,\theta} = 0$ for any values of l' except $l' = l$, $l \pm 2$, and $l \pm 4$.

$$\text{Case (b):} \quad I'_{3,\theta}(\Delta l, 2) = C_{l'}^{m+2} C_l^m \int_{-1}^{1} P_{l'}^{m+2} [x^2(1 - x^2)] P_l^m \, dx$$

The integration of equation (A27) over (-1,1) reduces the problem to the integration of equation (A25) over (-1,1) with $l' = l$, $l \pm 2$, and $l \pm 4$. The results are

$$I_3(0,2) = \frac{1}{4} \frac{\delta^2}{6} [I_{2,\theta}(0,2) - I'_{3,\theta}(0,2)]$$

$$\approx - \frac{1}{64 l^4} (l^4 - m^4) \delta^2 \qquad (A31a)$$

$$I_3(2,2) \approx \frac{1}{96 l^4} (l + m)^2 (l^2 - lm + m^2) \delta^2 \qquad (A31b)$$

$$I_3(-2,2) \approx \frac{1}{96 l^4} (l - m)^2 (l + lm + m^2) \delta^2 \qquad (A31c)$$

$$I_3(4,2) \approx - \frac{1}{384 l^4} (l + m)^3 (l - m) \delta^2 \qquad (A31d)$$

$$I_3(-4,2) \approx -\frac{1}{384l^4} (l+m)(l-m)^3\delta^2 \qquad (A31e)$$

Case (c): $I'_{3,\theta}(\Delta l,-2) = C_{l'}^{m-2}C_l^m \int_{-1}^{1} P_{l'}^{m-2}[x^2(1-x^2)]P_l^m \, dx$

To integrate over (-1,1) equation (A28) reduces the evaluation of $I'_{3,\theta}(\Delta l,-2)$ to repeated integrations of equation (A25) over (-1,1). Again, only the results will be given:

$$I_3(0,-2) \approx \frac{1}{64l^4} (l^4-m^4)\delta^2 \qquad (A32a)$$

$$I_3(2,-2) \approx -\frac{1}{96l^4} (l-m)^2(l^2+lm+m^2)\delta^2 \qquad (A32b)$$

$$I_3(-2,-2) \approx -\frac{1}{96l^4} (l+m)^2(l^2-lm+m^2)\delta^2 \qquad (A32c)$$

$$I_3(4,-2) \approx \frac{1}{384l^4} (l-m)^3(l+m)\delta^2 \qquad (A32d)$$

$$I_3(-4,-2) \approx -\frac{1}{384l^4} (l+m)^3(l-m)\delta^2 \qquad (A32e)$$

Case (d): $I_{3,\theta}(\Delta l,-4) = C_{l'}^{m-4}C_l^m \int_{-1}^{1} P_{l'}^{m-4}(1-x^2)^2P_l^m \, dx$

These integrals can be evaluated by integrating equation (A29) over (-1,1). This reduces the problem to repeated integrations, over (-1,1), of

$$P_l^m(1-x^2)P_l^{m-2} \approx \frac{1}{4l^2} \left(2P_l^m P_{l'}^m - P_l^m P_{l'+2}^m - P_l^m P_{l'-2}^m \right)$$

which is obtained by dividing equation (A28) by x^2. The expressions obtained are:

$$I_3(0,-4) \approx \frac{1}{256l^4} (l-m)^2(l+m)^2\delta^2 \qquad (A33a)$$

$$I_3(2,-4) \approx -\frac{1}{384l^4} (l-m)^3(l+m)\delta^2 \qquad (A33b)$$

53

$$I_3(-2,4) \approx \frac{1}{384l^4} (l-m)^3 (l+m) \delta^2 \qquad \text{(A33c)}$$

$$I_3(4,-4) \approx -\frac{1}{6 \times 256 l^4} (l-m)^4 \delta^2 \qquad \text{(A33d)}$$

$$I_3(-4,-4) \approx \frac{1}{6 \times 256 l^4} (l+m)^4 \delta^2 \qquad \text{(A33e)}$$

Case (e): $I_{3,\theta}(\Delta l, 4) = C_l^{m+4} C_l^m \int_{-1}^{1} P_l^{m+4} (1-x^2)^2 P_l^m \, dx$

Evaluation of these integrals by methods shown earlier gives

$$I_3(0,4) \approx \frac{1}{256 l^4} (l^2 - m^2)^2 \delta^2 \qquad \text{(A34a)}$$

$$I_3(2,4) \approx -\frac{1}{384 l^4} (l+m)^3 (l-m) \delta^2 \qquad \text{(A34b)}$$

$$I_3(-2,4) \approx \frac{1}{384 l^4} (l-m)^3 (l+m) \delta^2 \qquad \text{(A34c)}$$

$$I_3(4,4) \approx \frac{1}{6 \times 256 l^4} (l+m)^4 \delta^2 \qquad \text{(A34d)}$$

$$I_3(-4,4) \approx \frac{1}{6 \times 256 l^4} (l-m)^4 \delta^2 \qquad \text{(A34e)}$$

This completes the evaluation of I_3 for all allowed combinations of Δm and Δl, and makes it possible to write expressions for the overlap integral (eq. (A1))

$$\beta(v,l,m;v+\Delta v,l+\Delta l,m+\Delta m) = \frac{\delta^2}{\sinh \delta} \frac{\sqrt{v+1,0}}{2L\sqrt{\alpha}} (I_2 + I_3)$$

For example,

$$\beta(v,l,m;v+\Delta v,l,m) = \beta(\Delta v,0,0) = \frac{\delta^2}{\sinh \delta} \frac{\sqrt{v+1,0}}{2L\sqrt{\alpha}} \left[\frac{l^2+m^2}{4l^2} + \frac{1}{128 l^4} (3l^4 + 2l^2 m^2 + 3m^4) \delta^2 \right]$$

54

COMBINATION OF THE $\overline{\beta^2}(\Delta v, \Delta l, \Delta m)$

The expression for the overlap integral is dependent on m ($l,\ldots,-2,-1,0 = m = 1,2,\ldots,l$) and yet the energy of the molecule is independent of m, which only describes the orientation of the angular momentum vector. Therefore, an average, over all possible values of m is more appropriate for use in energy exchange problems. However, it is not β but β^2 that is proportional to the transition probability, and the average $\overline{\beta^2}$ over all possible m will be sought.

This average $\overline{\beta^2}$ will be found subject to the assumption that $l \gg 1$, since $I_2(\Delta l, \Delta m)$ and $I_3(\Delta l, \Delta m)$ have been derived on the basis of this assumption.

$$\overline{\beta^2}(\Delta v, \Delta l, \Delta m) = \frac{1}{2l+1} \sum_{m=-l}^{m=l} \beta^2(\Delta v, \Delta l, \Delta m) \tag{A35}$$

The sum on the right of this equation can be found exactly, but the same results are arrived at by writing

$$\overline{\beta^2}(\Delta v, \Delta l, \Delta m) \approx \frac{1}{2l} \int_{-l}^{l} \beta^2(\Delta v, \Delta l, \Delta m)\, dm$$

The average $\overline{\beta^2}$ is, of course, independent of m.

Instead of deriving $\overline{\beta^2}(\Delta v, \Delta l, \Delta m)$ for each possible combination of Δl and Δm, one such derivation will be made, and the result of this same procedure applied to the other combinations will be stated. The example chosen is $\beta(\Delta v, 0, 0)$, whose square is

$$\beta^2(\Delta v, 0, 0) = K \left\{ \frac{(l^2+m^2)^2}{16 l^4} + \frac{1}{256 l^6} \left[(l^2+m^2)(3l^4+2l^2 m^2+3m^4) \right] \delta^2 \right.$$

$$\left. + \frac{1}{128 l^8} (9l^8+12l^6 m^2+18l^4 m^4+12l^2 m^6+9m^8)\delta^4 \right\} \tag{A36}$$

where

$$K = \left(\frac{\delta^2}{\sinh \delta} \right)^2 \left(\frac{v+1,0}{4L^2 \alpha} \right)$$

Then

55

$$\overline{\beta^2}(\Delta v,0,0) = \frac{1}{2l} \int_{-l}^{l} \beta^2(\Delta v,0,0)\, dm$$

$$\approx K \left(\frac{7}{60} + \frac{1}{42}\,\delta^2 + \frac{11}{8960}\,\delta^4\right) \tag{A36}$$

In a completely analogous way, the averaged squares below can be found.

$$\overline{\beta^2}(\Delta v,0,2) = \overline{\beta^2}(\Delta v,0,-2) = \overline{\beta^2}(\Delta v,2,0) = \overline{\beta^2}(\Delta v,-2,0) = K\left(\frac{1}{2^3\cdot 3\cdot 5} + \frac{\delta^2}{2^2\cdot 3\cdot 5\cdot 7} + \frac{\delta^4}{2^7\cdot 3^2\cdot 5}\right) \tag{A37}$$

$$\overline{\beta^2}(\Delta v,0,4) = \overline{\beta^2}(\Delta v,0,-4) = \overline{\beta^2}(\Delta v,4,0) = \overline{\beta^2}(\Delta v,-4,0) = K\left(\frac{\delta^4}{2^9\cdot 3^2\cdot 5\cdot 7}\right) \tag{A38}$$

$$\overline{\beta^2}(\Delta v,2,2) = \overline{\beta^2}(\Delta v,-2,-2) = K\left(\frac{31}{2^8\cdot 5} + \frac{367\delta^2}{2^9\cdot 3\cdot 5\cdot 7} + \frac{5633\delta^4}{2^{12}\cdot 3^4\cdot 5\cdot 7}\right) \tag{A39}$$

$$\overline{\beta^2}(\Delta v,2,-2) = \overline{\beta^2}(\Delta v,-2,2) = K\left(\frac{1}{2^8\cdot 5} + \frac{17\delta^2}{2^9\cdot 3\cdot 5\cdot 7} + \frac{383\delta^4}{2^{12}\cdot 3^4\cdot 5\cdot 7}\right) \tag{A40}$$

$$\overline{\beta^2}(\Delta v,2,4) = \overline{\beta^2}(\Delta v,4,2) = \overline{\beta^2}(\Delta v,-2,-4) = \overline{\beta^2}(\Delta v,-4,-2) = K\left(\frac{233\delta^4}{2^{15}\cdot 3^4\cdot 7}\right) \tag{A41}$$

$$\overline{\beta^2}(\Delta v,2,-4) = \overline{\beta^2}(\Delta v,-4,2) = \overline{\beta^2}(\Delta v,4,-2) = \overline{\beta^2}(\Delta v,-2,4) = K\left(\frac{23\delta^4}{2^{15}\cdot 3^4\cdot 7}\right) \tag{A42}$$

$$\overline{\beta^2}(\Delta v,4,-4) = \overline{\beta^2}(\Delta v,-4,4) = K\left(\frac{\delta^4}{2^{18}\cdot 3^4}\right) \tag{A43}$$

$$\overline{\beta^2}(\Delta v,4,4) = \overline{\beta^2}(\Delta v,-4,-4) = K\left(\frac{511\delta^4}{2^{18}\cdot 3^4}\right) \tag{A44}$$

Each of the squares $\overline{\beta^2}(\Delta v,\Delta l,\Delta m)$ is proportional to the transition probability $P(\Delta v,\Delta l,\Delta m)$. The total transition probability, for all possible values of Δm is given by

$$P(\Delta v,\Delta l) = \sum_{\Delta m} P(\Delta v,\Delta l,\Delta m)$$

Consequently, the constant, $\beta^2(\Delta v,\Delta l)$ to be used in computing this transition probability is

$$\beta^2(\Delta v, \Delta l) = \sum_{\Delta m} \overline{\beta^2}(\Delta v, \Delta l, \Delta m)$$

and when these sums are carried out, using the results of equations (A37) through (A44), it is found that

$$\beta^2(\pm 1, 0) = K\left(\frac{2}{15} + \frac{1}{35}\delta^2 + \frac{1}{630}\delta^4\right)$$

$$\beta^2(\pm 1, \pm 2) = K\left(\frac{1}{30} + \frac{1}{105}\delta^2 + \frac{2}{2835}\delta^4\right)$$

$$\beta^2(\pm 1, \pm 4) = K\left(\frac{\delta^4}{22,680}\right)$$

where

$$K = \left(\frac{\delta^2}{\sinh\,\delta}\right)^2\left[\frac{m\hbar\omega(v+1,0)}{16\mu E_c}\right] = \left(\frac{\delta^2}{\sinh\,\delta}\right)^2\left(\frac{v+1,0}{4L^2\alpha}\right)$$

and $(v+1,0) = v+1$ or v accordingly as $\Delta v = \pm 1$.

APPENDIX B

CALCULATION OF COLLISION IMPULSE FOURIER TRANSFORMS

A slightly asymmetric collision perturbation of the form

$$U(t) = U_o e^{qt} \operatorname{sech}^2 at \tag{B1}$$

has been used to account for the effects of irreversible excitation of vibrational energy during collision. The dimensionless Fourier transform of this impulse is

$$F^* = \omega \int_{-\infty}^{\infty} e^{qt} \operatorname{sech}^2(at) e^{i\omega t} \, dt \tag{B2}$$
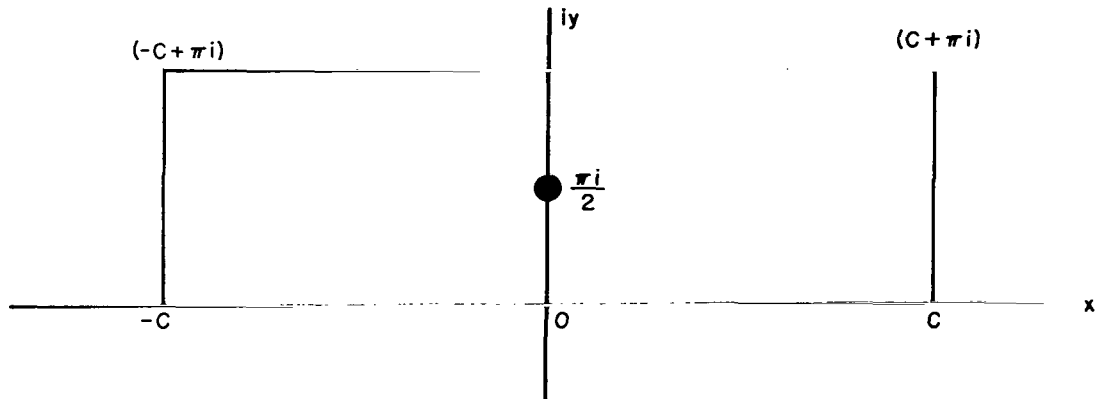
This integral, which can be written

$$F^* = \frac{\omega}{a} \int_{-\infty}^{\infty} e^{(q/a)x} \operatorname{sech}^2 x \, e^{i(\omega/a)x} \, dx \tag{B3}$$

will be evaluated by contour integration. Accordingly, we integrate the complex integral

$$\oint e^{(q/a)z} \operatorname{sech}^2 z \, e^{(i\omega/a)z} \, dz$$

about the rectangular path shown in the sketch. The integrand is analytic at all points interior to this contour except at the pole $z = (\pi i/2)$. Consequently,

$$\int_{-c}^{c} e^{qx/a} \operatorname{sech}^2 x \, e^{i(\omega/a)x} \, dx + i \int_{0}^{\pi} e^{(q/a)(c+iy)} \operatorname{sech}^2(c+iy) e^{(i\omega/a)(c+iy)} \, dy$$

$$+ \int_{c}^{-c} e^{(q/a)(x+\pi i)} \operatorname{sech}^2(x + \pi i) e^{(i\omega/a)(x+\pi i)} \, dx$$

$$+ i \int_{\pi}^{0} e^{(q/a)(-c+iy)} \operatorname{sech}^2(-c + iy) e^{(i\omega/a)(-c+iy)} \, dy = 2\pi i \left[\text{Residue at } \frac{\pi i}{2} \right] \quad (B4)$$

When we take $\lim\limits_{c \to \infty}$ of both sides of this equation, we get

$$\int_{-\infty}^{\infty} e^{(q/a)x} \operatorname{sech}^2 x \, e^{(i\omega/a)x} \, dx \left[1 - e^{(\pi/a)(q_i - \omega)} \right]$$

$$+ i \lim_{c \to \infty} \int_{0}^{\pi} e^{(q/a)(c+iy)} \operatorname{sech}^2(c + iy) e^{(i\omega/a)(c+iy)} \, dy$$

$$+ i \lim_{c \to \infty} \int_{\pi}^{0} e^{(q/a)(-c+iy)} \operatorname{sech}^2(-c + iy) e^{(i\omega/a)(-c+iy)} \, dy = 2\pi i \left[\text{Residue at } \frac{\pi i}{2} \right]$$

$$(B5)$$

Since $\operatorname{sech}^2 z = 1 + \tanh^2 z$, and $\lim\limits_{z \to \infty} \tanh z = 1$, it is clear that

$$\lim_{c \to \infty} \left| \int_{\pi}^{0} e^{(q/a)(-c+iy)} \operatorname{sech}^2(-c + iy) e^{(i\omega/a)(-c+iy)} \, dy \right|$$

$$\leq \lim_{c \to \infty} \pi \left| e^{(q/a)(-c+iy)} [1 + \tanh^2(-c + iy)] e^{(i\omega/a)(-c+iy)} \right| = 0 \quad (B6)$$

The second integral in equation (B5) is treated by writing its integrand in terms of exponentials.

$$g(y) = e^{(q/a)(c+iy)} \operatorname{sech}^2(c + iy) e^{(i\omega/a)(c+iy)} = \frac{4e^{[(q/a)-2+(i\omega/a)](c+iy)}}{1 + 2e^{-2(c+iy)} + e^{-4(c+iy)}}$$

$$(B7)$$

Since $(q/a) \ll 1$, it follows that $(q/a) - 2 < 0$ and therefore $\lim_{c \to \infty} g(y) = 0$. Hence,

$$\lim_{c \to \infty} \left| \int_{0}^{\pi} e^{(q/a)(c+iy)} \operatorname{sech}^2(c + iy) e^{(i\omega/a)(c+iy)} \, dy \right| \leq \lim_{c \to \infty} \pi |g(y)| = 0 \qquad \text{(B8)}$$

and equation (B5) becomes

$$\int_{-\infty}^{\infty} e^{(q/a)x} \operatorname{sech}^2 x \, e^{(i\omega/a)x} \, dx = \frac{2\pi i \left[\text{Residue at } \frac{\pi i}{2} \right]}{\left[1 + e^{(\pi/a)(q_i - \omega)} \right]} \qquad \text{(B9)}$$

In order to find the residue of

$$f(z) = e^{(q/a)z} \operatorname{sech}^2 z \, e^{(i\omega/a)z}$$

at $z = \pi i$, it is of help to write

$$f(z) = \frac{e^{[(q-i\omega)/a]z}}{\cosh^2 z} = \frac{p(z)}{q(z)}$$

where both $p(z)$ and $q(z)$ are analytic at $z = \pi i/2$, and can therefore be expanded about that point.

$$f(z) = \frac{p\left(\frac{\pi i}{2}\right) + p'\left(\frac{\pi i}{2}\right)\left(z - \frac{\pi i}{2}\right) + \frac{p''(\pi i/2)}{2}\left(z - \frac{\pi i}{2}\right)^2 + \ldots}{\left(z - \frac{\pi i}{2}\right)^2 \left[\frac{q''(\pi i/2)}{2} + \frac{q'''(\pi i/2)}{6}\left(z - \frac{\pi i}{2}\right) + \ldots \right]} \qquad \text{(B10)}$$

If we carry out the division of the series, we obtain

$$f(z) = \frac{p\left(\frac{\pi i}{2}\right)}{\left(z - \frac{\pi i}{2}\right)^2} + \frac{\left\{ \frac{2p'(\pi i/2)}{q''(\pi i/2)} - \frac{2}{3} \frac{p(\pi i/2)q'''(\pi i/2)}{[q''(\pi i/2)]^2} \right\} + \ldots}{\left(z - \frac{\pi i}{2}\right)} \qquad \text{(B11)}$$

and the residue is given by

60

Residue at $\frac{\pi i}{2} = \left\{ \frac{2p'\left(\frac{\pi i}{2}\right)}{q''\left(\frac{\pi i}{2}\right)} - \frac{2}{3} \frac{p\left(\frac{\pi i}{2}\right) q'''\left(\frac{\pi i}{2}\right)}{\left[q''\left(\frac{\pi i}{2}\right) \right]^2} \right\} = - \left(\frac{q + i\omega}{a} \right) e^{\left[(q+i\omega/a) \right](\pi i/2)}$

Finally,

$$F^* = \frac{\omega}{a} \int_{-\infty}^{\infty} e^{(q/a)x} \; \text{sech}^2 \; x \; e^{(i\omega/a)x} \; dx = \frac{\frac{-2\omega\pi i}{a} \left(\frac{q + i\omega}{a} \right) e^{\left[(q+i\omega)/a \right](\pi i/2)}}{1 - e^{\left[(q+i\omega)/a \right]\pi i}}$$

(B12)

and for $(\pi\omega/a) \gg 1$, this gives

$$F^* = + \frac{2\pi\omega}{a^2} (\omega - iq) e^{-(\pi\omega/2a)}$$

so that

$$|F^*|^2 = 4\pi^2 \left(\frac{\omega}{a} \right)^4 e^{-(\pi\omega/a)} \left(1 + \frac{q^2}{\omega^2} \right)$$

(B13)

The factor $[1 + (q^2/\omega^2)]$ represents the correction to the usual adiabatic collision transition probability, which is due to the asymmetrical factor e^{qt} in the impulse function.

APPENDIX C

VIBRATIONAL ENERGY AND ITS DERIVATIVES AT THE

COLLISION TURNING POINT

Consider a diatomic molecule subject to the perturbation

$$U = U_e + \frac{1}{2} (\text{grad } U)_e \, y \tag{C1}$$

where $y = (\rho - \rho_e)$, the oscillator coordinate. When the molecule is initially at rest ($y_i = 0$), the maximum amplitude of classical motion induced at any time t is, according to Green's method

$$y_m = \left[\int_{-\infty}^{t} \frac{(\text{grad } U)_e}{2\mu\omega} \cos \omega\tau \, d\tau \right]^2 + \left[\int_{-\infty}^{t} \frac{(\text{grad } U)_e}{2\mu\omega} \sin \omega\tau \, d\tau \right]^2$$

so that

$$y_m = \left| \int_{-\infty}^{t} \frac{(\text{grad } U)_e}{2\mu\omega} e^{i\omega t} \, dt \right| \tag{C2}$$

The net amount of vibrational energy excited is, in units of $\hbar\omega$

$$\varepsilon = \frac{\Delta E}{\hbar\omega} = \frac{\mu\omega^2 y_m^2}{2\hbar\omega} = \frac{1}{8\mu\hbar\omega} \left| \int_{-\infty}^{t} (\text{grad } U)_e \, e^{i\omega t} \, dt \right|^2 \tag{C3}$$

This classical result is exactly the same as the quantum probability of transition $0 \leftrightarrow 1$ given by small perturbation theory

$$\varepsilon = P_{01} = \left| \frac{1}{\hbar} \int_{-\infty}^{t} H_{01} \, e^{i\omega t} \, dt \right|^2 \tag{C4}$$

where H_{01} is the harmonic oscillator matrix element

$$H_{01} = \left\langle \psi_1^* | U | \psi_0 \right\rangle = \left(\frac{\hbar}{8\mu\omega} \right)^{1/2} (\text{grad } U)_e \tag{C5}$$

When the transition probability becomes too large for small perturbation methods to apply, Kerner's solutions of Schrödinger's equation are used. The probability of transition $m \to n$ due to a forcing function acting on a harmonic oscillator is found to be (ref. 24)

$$P_{mn}(t) = m! n! \, e^{-\varepsilon} \varepsilon^{m+n} S_{mn}^2 (\varepsilon) \tag{C6}$$

where the polynomial S_{mn} is

$$S_{mn}(\varepsilon) = \sum_{j=0}^{m < n} \frac{(-1)^j e^{-j}}{(n - j)! j! (m - j)!} \tag{C7}$$

For present purposes, transitions from the ground state are of interest.

$$P_{on} = \frac{\varepsilon^n e^{-\varepsilon}}{n!} \tag{C8}$$

Note that P_{01} reduces to the usual small perturbation result (eq. (C4)) when ε is small. Also the sum of all P_{on} is unity as it should be. The total energy in all vibrational modes is

$$V = \hbar\omega \sum_{n=0}^{\infty} n P_{on} = \hbar\omega e^{-\varepsilon} \sum_{n=1}^{\infty} \frac{\varepsilon^n}{(n - 1)!} = \hbar\omega\varepsilon \tag{C9}$$

Where the interaction potential is exponential, (grad U) = U/L and equation (C9) can be expressed

$$\frac{V(t)}{\hbar\omega} = \varepsilon = \left| \frac{\beta_{01}}{\hbar} \int_{-\infty}^{t} U_e(t) e^{i\omega t} \, dt \right|^2 \tag{C10}$$

which is the result used in equation (109). Hereafter, we shall drop the subscripts on β and U for convenience.

The vibrational energy at $t = 0$ is

$$V_0 = \frac{\beta\omega^2}{\hbar} \left\{ \left| \int_{-\infty}^{0} U \cos \omega t \, dt \right|^2 + \left| \int_{-\infty}^{0} U \sin \omega t \, dt \right|^2 \right\} \tag{C11}$$

The first integral on the right is negligibly small compared with the second. The latter can be treated by repeated integration by parts to give

$$\int_{-\infty}^{0} U \sin \omega t \, dt = - \frac{U_0}{\omega} + \frac{\ddot{U}_0}{\omega^3} - \frac{\ddddot{U}_0}{\omega^5} + \ldots \simeq - \frac{U_0}{\omega} \tag{C12}$$

where we have used the fact that U and all its derivatives vanish at $|t| = \infty$. Thus, to terms of first order in ω^{-1}

$$V_0 = \frac{\beta^2 U_0{}^2}{\hbar \omega} \tag{C13}$$

The derivatives of V at $t = 0$ are obtained by differentiation of equation (C10). The cosine transform of U and all odd derivatives of U at $t = 0$ are taken to vanish

$$\int_{-\infty}^{0} U \cos \omega t \, dt = \dot{U}_0 = \dddot{U}_0 = 0 \tag{C14}$$

which is equivalent to neglect of asymmetrical terms in U and V. Then the results are

$$\dot{V}_0 = \ddot{V}_0 = \dddot{V}_0 = 0 \tag{C15}$$

$$\ddddot{V}_0 = \frac{2\beta^2 \omega}{\hbar} U_0 \ddot{U}_0 \tag{C16}$$

The vibrational energy at the turning point is seen to vary essentially as t^4. These results are valid for any impulse function $U(t)$ where the duration of impulse is long compared with ω^{-1}, provided only that U varies exponentially with distance between the collision partners. Similar relations obtain in the more general case, only U is then replaced by $(L \text{ grad } U)$.

REFERENCES

1. Benson, S. W.; and Fueno, T.: Mechanism of Atom Recombination by Consecutive Vibrational Deactivations. J. Chem. Phys., vol. 36, 1962, p. 1597.

2. Treanor, C. E.; and Marrone, P. V.: Effect of Dissociation on the Rate of Vibrational Relaxation. Phys. Fluids, vol. 5, 1962, p. 1022.

3. Keck, J.; and Carrier, G.: Diffusion Theory of Nonequilibrium Dissociation and Recombination. J. Chem. Phys., vol. 43, 1965, p. 2284.

4. Landau, L.; and Teller, E.: Contribution to the Theory of Sound Dispersion. Physik Z. Sowjetunion, vol. 10, 1936, p. 34.

5. Blackman, V.: Vibrational Relaxation in Oxygen and Nitrogen. J. Fluid Mech., vol. 1, 1956, p. 61.

6. Millikan, R. C.; and White, D. R.: Vibrational Energy Exchange Between N_2 and CO. J. Chem. Phys., vol. 39, 1963, p. 98.

7. Millikan, R. C.; and White, D. R.: Systematics of Vibrational Relaxation. J. Chem. Phys., vol. 39, 1963, p. 3209.

8. Appleton, J. P.; and Steinberg, M.: Vacuum-Ultraviolet Absorption of Shock-Heated Vibrationally Excited Nitrogen. J. Chem. Phys., vol. 46, 1967, p. 1521.

9. Appleton, J. P.: Shock-Tube Study of the Vibrational Relaxation of Nitrogen Using Vacuum-Ultraviolet Light Absorption. J. Chem. Phys., vol. 47, 1967, p. 3231.

10. Bethe, H. A.; and Teller, E.: Deviations From Thermal Equilibrium in Shock Waves. Aberdeen Proving Ground Ballistics Research Lab Rep. X-117, 1945.

11. Schwartz, R. N.; Slawsky, Z. I.; and Herzfeld, K. F.: Calculation of Vibrational Relaxation Times in Gases. J. Chem. Phys., vol. 20, 1952, p. 1591.

12. Zener, C.: Low Velocity Inelastic Collisions. Phys. Rev., vol. 38, 1931, p. 277.

13. Zener, C.: Some Observations on the Theory of Interchange of Vibrational and Translational Energy. Proc. Cambridge Phil. Soc., vol. 29, 1933, p. 136.

14. Jackson, J. M.; and Mott, N. F.: Energy Exchange Between Inert Gas Atoms and a Solid Surface. Proc. Roy. Soc. London, ser. A137, 1932, p. 703.

15. Takayanagi,K.: On the Inelastic Collisions Between Molecules, I. Prog. Theor. Phys. Japan, vol. 8, 1952, p. 111.

16. Schwartz, R. N.; and Herzfeld, K. F.: Vibrational Relaxation Times in Gases (Three-Dimensional Treatment). J. Chem. Phys., vol. 22, 1954, p. 767.

17. Mott, N. F.; and Massey, H. S. W.: The Theory of Atomic Collisions. 2nd ed., Ch. VIII, Clarendon Press, Oxford, 1949, §5.

18. Treanor, C. E.; Rich, J. W.; and Rehm, R. G.: Vibrational Relaxation of Anharmonic Oscillators With Exchange-Dominated Collisions. J. Chem. Phys., vol. 48, 1968, p. 1798.

19. Rapp, D.: Complete Classical Theory of Vibrational Energy Exchange. J. Chem. Phys., vol. 32, 1960, p. 735.

20. Herzfeld, K. F.: Relaxation Phenomena in Gases. Sec. H of Thermodynamics and Physics of Matter, Princeton Univ. Press, 1955, p. 646.

21. Rapp, D.; and Sharp, T. E.: Vibrational Energy Transfer in Molecular Collisions Involving Large Transition Probabilities. J. Chem. Phys., vol. 38, 1963, p. 2641.

22. Sharp, T. E.; and Rapp, D.: Evaluation of Approximations Used in the Calculation of Excitation by Collision. I. Vibrational Excitation of Molecules. J. Chem. Phys., vol. 43, 1965, p. 1233.

23. Rapp, D.; and Englander-Golden, P.: Resonant and Near-Resonant Vibrational-Vibrational Energy Transfer Between Molecules in Collisions. J. Chem. Phys., vol. 40, 1964, pp. 573, 3120.

24. Kerner, E. H.: Note on the Forced and Damped Oscillator in Quantum Mechanics. Can. J. Phys., vol. 36, 1958, p. 371.

25. Treanor, C. E.: Vibrational Energy Transfer in High-Energy Collisions. J. Chem. Phys., vol. 43, 1965, p. 532.

26. Treanor, C. E.: Transition Probabilities for the Forced Harmonic Oscillator. J. Chem. Phys., vol. 44, 1966, p. 2220.

27. Calvert, J. B.; and Amme, R. C.: Three-Dimensional Morse-Potential Calculations of Vibrational Energy Transfer: Application to Diatomic Molecules. J. Chem. Phys., vol. 45, 1966, p. 4710.

28. Mies, F. H.; and Shuler, K. E.: Quantum-Mechanical Calculation of Harmonic Oscillator Transition Probabilities. II. Three-Dimensional Impulsive Collisions. J. Chem. Phys., vol. 37, 1962, p. 177.

29. Shuler, K. E.; and Zwanzig, R.: Quantum-Mechanical Calculation of Harmonic Oscillator Transition Probabilities in a One-Dimensional Impulsive Collision. J. Chem. Phys., vol. 33, 1960, p. 1778.

30. Meador, W. E.: The Interactions Between Nitrogen and Oxygen Molecules. NASA TR R-68, 1960.

31. Shields, F. Douglas: Sound Absorption in the Halogen Gases. J. Acoust. Soc. Am., vol. 32, 1960, p. 180.

32. Hirschfelder, J. O.; Curtis, C. F.; and Bird, R. B.: Molecular Theory of Gases and Liquids. John Wiley and Sons, Inc., New York, N. Y. 1954, p. 1111.

33. Benson, S. W.; and Berend, G. C.: Vibrational Relaxation of Diatomic Molecules. J. Chem. Phys., vol. 44, 1966, p. 470.

34. Mason, E. A.; and Vanderslice, J. T.: Delta-Function Model for Short-Range Intermolecular Forces. I. Rare Gases. J. Chem. Phys., vol. 28, 1958, p. 432.

35. Vanderslice, J. T.; Mason, E. A.; and Lippincott, E. R.: Interactions Between Ground-State Nitrogen Atoms and Molecules. The N-N, $N-N_2$, and N_2-N_2 Interactions. J. Chem. Phys., vol. 30, 1959, p. 129.

36. Amdur, I.; Mason, E. A.; and Jordan, J. E.: Scattering of High Velocity Neutral Particles. X. $He-N_2$; $A-N_2$. The N_2-N_2 Interaction. J. Chem. Phys., vol. 27, 1957, p. 527.

37. Herzfeld, K. F.; and Litovitz, T. A.: Absorption and Dispersion of Ultrasonic Waves. Academic Press, N. Y., 1959, p. 303.

38. Sansone, G.: Orthogonal Functions. Interscience Pub. Co., N. Y., 1959.

"*The aeronautical and space activities of the United States shall be
conducted so as to contribute . . . to the expansion of human knowl-
edge of phenomena in the atmosphere and space. The Administration
shall provide for the widest practicable and appropriate dissemination
of information concerning its activities and the results thereof.*"

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and
technical information considered important,
complete, and a lasting contribution to existing
knowledge.

TECHNICAL NOTES: Information less broad
in scope but nevertheless of importance as a
contribution to existing knowledge.

TECHNICAL MEMORANDUMS:
Information receiving limited distribution
because of preliminary data, security classifica-
tion, or other reasons.

CONTRACTOR REPORTS: Scientific and
technical information generated under a NASA
contract or grant and considered an important
contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information
published in a foreign language considered
to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information
derived from or of value to NASA activities.
Publications include conference proceedings,
monographs, data compilations, handbooks,
sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION
PUBLICATIONS: Information on technology
used by NASA that may be of particular
interest in commercial and other non-aerospace
applications. Publications include Tech Briefs,
Technology Utilization Reports and Notes,
and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546